

# Synthesis and Structure of 1,3-Diisopropyl-4,5-dimethylimidazolium *N,N'*-Diphenylureate [1]

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*Dedicated to Professor Dietrich Döpp on the occasion of his 65th birthday*

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1,3-Diisopropyl-4,5-dimethylimidazolium diphenylureate (**4**) has been obtained from 2,3-dihydro-1,3-diisopropyl-3,4-dimethylimidazol-2-ylidene (**3**) and *N,N'*-diphenylurea in good yield. The crystal structure of **4** contains dimeric ureate anions linked by unsymmetrical NHN hydrogen bonds while only weak interactions are detected between the imidazolium cations and the anions.

## Introduction

2*H*-Imidazolium salts have drawn much attention in recent years owing to their ionic liquid properties [2]. In addition to an “unsymmetrical” substitution pattern, hydrogen bridging to the counter ion (**1**) seems to be helpful to generate a low melting point.

In the course of our investigations on imidazole derivatives, we isolated and characterised several compounds of the type **1** in which hydrogen bridging could be proved by structure analyses for X = Cl [3], Br [4], I [5], S<sub>2</sub>O<sub>7</sub> [6], SnCl<sub>3</sub> [7], PdCl<sub>4</sub> [8]. On the other hand, weak and hard counterions (X = HF<sub>2</sub> [9], BF<sub>4</sub> [10]) lead to the ionic type solid state structure **2**. Therefore, it is generally concluded that coordinating anions form type **1** salts preferently.

## Crystal Structure of 1,3-Diisopropyl-4,5-dimethylimidazolium *N,N'*-Diphenylureate

We obtained the title compound **4** through the reaction of 2,3-dihydro-1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene (**3**) and *N,N'*-diphenylurea in acetone as colourless crystals in good yield. The crystal structure of the acetone solvate **4** × C<sub>3</sub>H<sub>6</sub>O (Figs. 1 and 2, Tables 1 and 2) reveals the presence of dimeric diphenyl ureate ions connected *via* unsymmetrical NHN' hydrogen bridges [N(5)-H(5) 0.89(2), H(5)-N(7) 2.07(4), N(8)-H(8) 0.92(2), H(8)-N(6) 2.06(4) Å; N(5)-H(5)-N(7) 172(1), N(8)-

Table 1. Crystal data and structure refinement for C<sub>51</sub>H<sub>70</sub>N<sub>8</sub>O<sub>3</sub> (**4** × C<sub>3</sub>H<sub>6</sub>O).

Empirical formula	C <sub>51</sub> H <sub>70</sub> N <sub>8</sub> O <sub>3</sub>
Formula weight	843.15
Temperature	173(2) K
Wavelength	0.71073 Å
Crystal system	monoclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>
Unit cell dimensions	<i>a</i> = 14.936(6) Å <i>b</i> = 25.088(8) Å <i>c</i> = 14.624(7) Å <i>β</i> = 117.72(3)°
Volume	4851(3) Å <sup>3</sup>
<i>Z</i>	4
Density (calculated)	1.155 mg/mm <sup>3</sup>
Absorption coefficient	0.073 mm <sup>-1</sup>
<i>F</i> (000)	1824
Crystal size	0.4 × 0.5 × 0.4 mm <sup>3</sup>
<i>θ</i> Range for data collect.	2.79 to 27.53°
Index ranges	-16 ≤ <i>h</i> ≤ 17, -32 ≤ <i>k</i> ≤ 32, -19 ≤ <i>l</i> ≤ -1
Reflections collected	19219
Independent reflections	10018 [ <i>R</i> (int) = 0.0521]
Completen. to <i>θ</i> = 27.53°	89.6 %
Absorption correction	none
Refinement method	Full-matrix least-squares on <i>F</i> <sup>2</sup>
Data / restraints / params	10018 / 0 / 818
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.032
Final <i>R</i> indices [ <i>I</i> > 2σ( <i>I</i> )]	<i>R</i> 1 = 0.0541, <i>wR</i> 2 = 0.1373
<i>R</i> Indices (all data)	<i>R</i> 1 = 0.0802, <i>wR</i> 2 = 0.1534
Extinction coefficient	0.0117(10)
Largest diff. peak and hole	0.455 and -0.380 e·Å <sup>-3</sup>

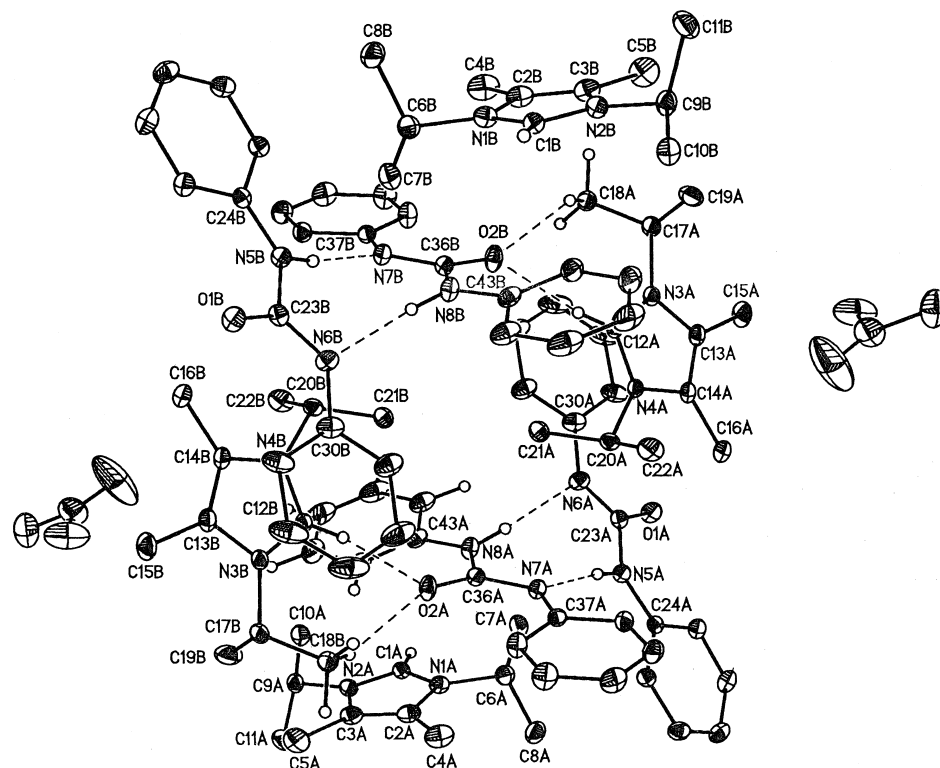


Fig. 1. Packing diagram of  $C_{51}H_{70}N_8O_3$  ( $4 \times C_3H_6O$ ). Ellipsoids of thermal vibration represent a 20% probability.

H(8)-N(6)  $175(1)^\circ$ ]. The planes of the two anionic fragments, defined as N(6)-C(23)-N(5) and N(7)-C(36)-N(8), form an interplanar angle of  $133.2(3)^\circ$ . As a consequence of the unsymmetrical nature of the NHN' hydrogen bonds, the urea fragments exhibit markedly different C-N bond lengths and O-C-N bond angles [C(23)-N(5)  $1.402(2)$ , C(23)-N(6)  $1.334(2)$ , C(36)-N(7)  $1.343(2)$ , C(36)-N(8)  $1.393(2)$  Å; O(1)-C(23)-N(5)  $119.8(2)$ , O(1)-C(23)-N(6)  $128.9(2)$ , O(2)-C(36)-N(7)  $128.6(2)$ , O(2)-C(36)-N(8)  $120.1(2)^\circ$ ]. These angles are widened as compared with the N-C-N angles [N(5)-C(23)-N(6)  $111.3(1)$ , N(7)-C(36)-N(8)  $111.3(1)^\circ$ ]. The C-O bond lengths are in the range expected for urea derivatives [C(23)-O(1)  $1.246(2)$ , C(36)-O(2)  $1.240(2)$  Å].

We observe only weak interactions between the imidazolium ions and the oxygen atoms of the dimeric anions which include the H atom at C2 of the imidazolium ring [C(12A)-H(1BA)  $0.95(2)$ , H(1BA)-O(2B)  $2.18(4)$  Å; C(12A)-H(1BA)-O(2B)  $167(1)^\circ$ ] and methyl H atoms of the isopropyl substituents [C(18A)-H(18A)  $1.02(2)$ , H(18A)-O(2B)  $2.18(3)$  Å; C(18A)-H(18A)-O(2B)  $139(1)$ , C(18A)-

Table 2. Selected bond lengths [Å] and angles [ $^\circ$ ] for  $C_{51}H_{70}N_8O_3$  ( $4 \times C_3H_6O$ ).

N(1)-C(1)	1.333(2)	N(1)-C(2)	1.392(2)
N(2)-C(1)	1.328(2)	N(2)-C(3)	1.392(2)
N(3)-C(12)	1.335(2)	N(3)-C(13)	1.381(2)
N(4)-C(12)	1.331(2)	N(4)-C(14)	1.388(2)
N(5)-C(24)	1.383(2)	N(5)-C(23)	1.402(2)
N(6)-C(23)	1.334(2)	N(6)-C(30)	1.397(2)
N(7)-C(36)	1.342(2)	N(7)-C(37)	1.393(2)
N(8)-C(43)	1.382(2)	N(8)-C(36)	1.394(2)
O(1)-C(23)	1.245(2)	O(2)-C(36)	1.239(2)
C(2)-C(3)	1.341(3)	C(13)-C(14)	1.354(3)
C(24)-N(5)-C(23)	128.00(14)	C(23)-N(6)-C(30)	122.07(15)
C(36)-N(7)-C(37)	121.76(13)	C(43)-N(8)-C(36)	126.87(15)
O(1)-C(23)-N(6)	128.94(15)	O(1)-C(23)-N(5)	119.75(17)
N(6)-C(23)-N(5)	111.31(14)	O(2)-C(36)-N(7)	128.59(15)
O(2)-C(36)-N(8)	120.12(15)	N(7)-C(36)-N(8)	111.28(13)

H(18B)-O(2B)  $141(4)^\circ$ ]. The geometry of the five-membered rings (Table 2) corresponds to that in the tetrafluoroborate salt [10]. The acetone molecules are not involved in hydrogen bonding.

Though NHN' hydrogen bonding has been studied extensively, the anion of N-cyano-N'-phenylurea, present in the salt **5** seems to be the only reported example for a dimeric anionic urea deriva-

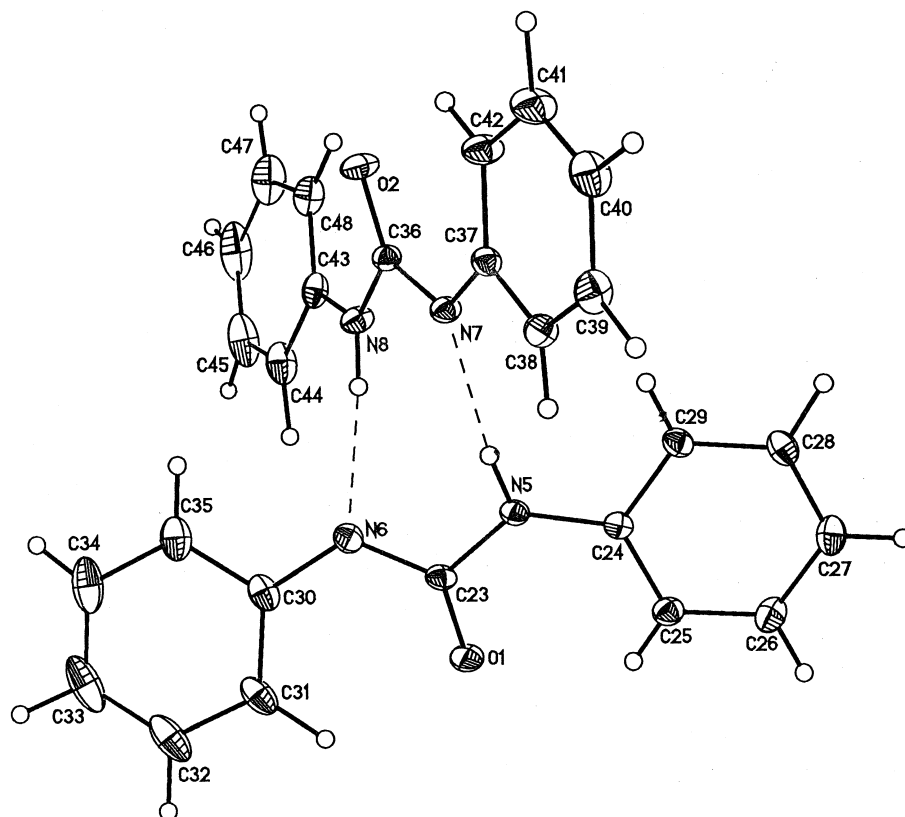


Fig. 2. View of the dianion of  $C_{51}H_{70}N_8O_3$  ( $4 \times C_3H_6O$ ). Ellipsoids of thermal vibration represent a 20% probability.

tive [11]. On comparison of the hydrogen bonding geometries, we observe a significant shortening of the  $N \cdots HN'$  bond [**4**: 2.06(4), 2.07(5); **5**: 2.26(4) Å] in **4** according to the higher basicity of the diphenylureate anion.

Hydrogen bonding in diphenylurea itself has been discussed [12]. Its crystal structure [13] consists of molecules linked by bifurcated N-H-O hydrogen bonding. A comparison with its structure shows for **4** almost identical distances in the C(O)N(H) fragment, while the N-C<sub>Ph</sub> distances are shortened markedly.

In summary, the crystal structure of **4** reveals the presence of dimeric ureate anions while only weak interactions including the imidazolium ions could be detected. Therefore, we conclude that the resulting dianions in **4** are only weak nucleophiles forming salts of the type **2** preferently.

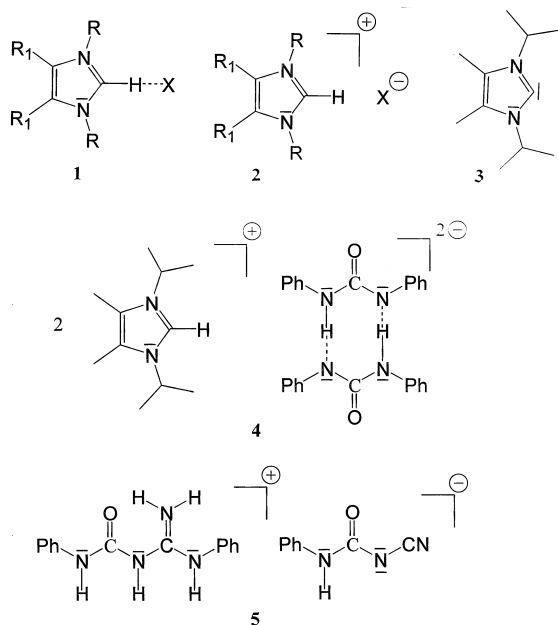
#### Experimental Section

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

imidazol-2-ylidene (**3**) has been prepared according to published procedures [14]. Crystals of  $4 \times C_3H_6O$  were obtained by slow evaporation of an acetone solution of **4** at room temperature.

#### 1,3-Diisopropyl-4,5-dimethylimidazolium *N,N'*-diphenylureate tetrahydrofuran solvate ( $4 \times C_4H_8O$ )

A solution of 1.27 g of **3** (7 mmol) in 20 ml of THF was added to 1.5 g (7 mmol) of *N,N'*-diphenylurea suspended in 20 ml of THF at 20 °C. After stirring for 15 min the precipitate was filtered off and dried *in vacuo*. Yield after recrystallisation from THF: 2.3 g (60%), colourless crystals, m. p. 110 °C. –  $^1H$  NMR (acetone- $d_6$ ):  $\delta$  = 1.45 (d, 12 H,  $CHMe_2$ ,  $^3J$  = 7 Hz), 1.71 (m, 2 H,  $OCH_2CH_2$ ), 2.24 (s, 6 H, 4,5-Me), 3.55 (m, 2 H,  $OCH_2CH_2$ ), 4.55 (sept, 2 H,  $CHMe_2$ ), 6.60 - 7.60 (m, 10 H, Ph), NH not observed. –  $^{13}C$  NMR (acetone- $d_6$ ):  $\delta$  = 8.1 (4,5-Me), 22.3 ( $CHMe_2$ ), 25.8 ( $OCH_2CH_2$ ), 50.8 ( $CHMe_2$ ), 57.7 ( $OCH_2CH_2$ ), 119.6 (C-4,5), 119.3, 127.1, 128.5, 144.9 (Ph), 156.9 (CO). – Analysis for  $C_{52}H_{72}N_8O_3$  (827.20): calcd. C 72.86, H 8.47, N 13.07; found C 71.39, H 9.17, N 12.73.



### Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC 193671 for compound **4**  $\times$   $C_3H_6O$ . Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ UK, Fax: +44-1223-336033; E-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>.

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