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Structural Changes of Di(2-pyridyl) Ketone on Single and Twofold Protonation

Hans Bock*, Tran T. H. Van, Holger Schödel, and Rüdiger Dienelt

Chemische Institute der Universität Frankfurt,
Marie-Curie-Straße 11, D-60439 Frankfurt, Germany

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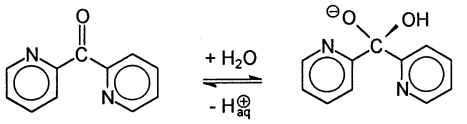
Di(2-pyridyl) ketone, intricately twisted due to its two n_N^{σ} and one n_O^{σ} lone pairs, exhibits tremendous structural differences on single and double protonation to salts containing either the anion $[B(C_6H_5)_4]^-$, which cannot be protonated, or Cl^-, which accepts two hydrogen bonds. In the monocation, generated in acetic acid with added sodium tetraphenylborate, the pyridine rings of di(2-pyridyl) ketone are planarized due to the formation of an intermolecular hydrogen bond. Aqueous hydrogen chloride produces a dication with both nitrogen centers protonated and the resulting di(2-pyridyl) ketone hydrate embedded in a complex hydrogen-bond network. Extensive quantum-chemical calculations based on the experimental structural data allow to rationalize the unexpected results.

The title compound, which is iso(valence)electronic with azodi(2-pyridine)[2], was first prepared in 1951 by treating 2-lithiopyridine with 2-cyanopyridine[3][4]. The acid−base reactions of di(2-pyridyl) ketone and its isomers have been investigated spectrophotometrically and the results discussed based on semiempirical calculations[5]. In aqueous solution, di(2-pyridyl) ketone (Eq. 2: M) remains unprotonated above pH = 5, is singly protonated exclusively at pH = 0 and diprotonated below pH = −5. The pH dependency of the UV absorption in aqueous solution (2) is discussed assuming hydration to its diol.



(1)

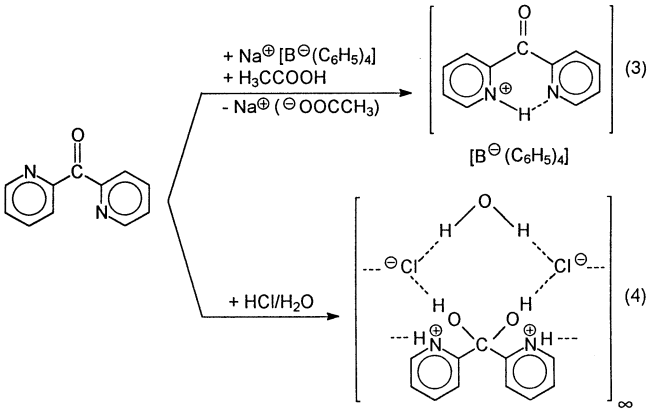
M(pH>5)		$MH^{\oplus}$(pH~0)		$MH_2^{\oplus\oplus}$(pH<-5)	
$\nu_m(cm^{-1})$	lgε	$\nu_m(cm^{-1})$	lgε	$\nu_m(cm^{-1})$	lgε
41300	3.93	<50000	>4.00	47200	3.94
36400	4.00	37600	4.23	35500	4.20
29400	2.33	28200	0.78	29400	2.11

(2)

For the keto form, which according to IR identification of the C−O stretch at 1667 cm^{-1} is not hydrated in aqueous solution[6][7] in the absence of metal cations[8], a pK value of 13.07 (25°C) has been approximated[6].

Di(2-pyridyl) ketone is used as the complexing ligand for spectrophotometric determination of numerous metal cations[5][8][9][10]. Structural studies of complexes containing transition-metal cations such as Ag^{I}[11], Au^{III}[12], Cu^{II}[8][13][14], Ni^{II}[8], Co^{III}[9], Cr^{III}[15], Ru^{II}[15], Pd^{II}[16], or Pt^{II}[17] demonstrate that the Me^{n+} contacts are established either at the pyridine nitrogen centers or with the geminal hydroxy groups (Eq. 3) and that the resulting six-membered ring often shows a tub conformation[6]. Surprisingly, a Cambridge Structural Database search[18] revealed that the structure of the parent di(2-pyridyl) ketone was unknown and of its proton adducts, only the one of a disordered 2-pyridinio 2-pyridyl ketone tetrafluoroborate.[11].

The obviously severe twisting of di(2-pyridyl) ketone[2] will be discussed further, based on the different prototype structures determined for two of its salts.



(3)

(4)

In the tetraphenylborate, di(2-pyridyl)amine is protonated between the two pyridyl nitrogen atoms and is monomeric due to the bulky anion. In contrast, the dichloride hydrate $[(Cl^-)_2(H_2O)]$ contains hydrogen bonds O−H···Cl^- to the chloride anions and is embedded in a polymeric hydrogen-bond network.

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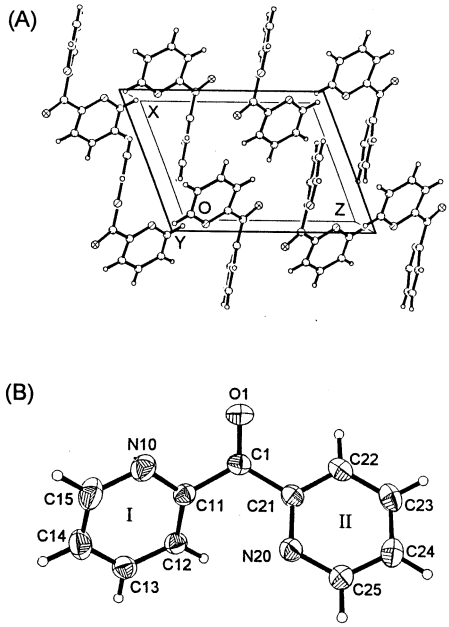
Crystal Structures

Differences between the molecular structures of di(2-pyridyl) ketone and the iso(valence)electronic azodi(2-pyridine) $H_4NC_5-N=N-C_5NH_4$[2] have already been analyzed in detail and will therefore only be summarized here for a discussion of the structural differences of the protonated ketone salts (3) and (4).

Di(2-pyridyl) Ketone

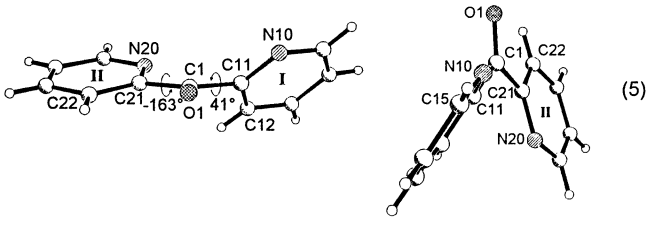
Di(2-pyridyl) ketone crystallizes from benzene solutions as colorless prisms (Experimental Section) which are monoclinic, $P2_1/n$, and contain $Z = 4$ molecules within the unit cell (Figure 1: A).

Figure 1. Crystal structure of di(2-pyridyl) ketone at 200 K: (A) Unit cell (monoclinic, $P2_1/n$, $Z = 4$) in y direction and (B) molecular structure (50% thermal ellipsoids) with numbering



In the crystallographic x,y plane, the molecules are arranged in a herringbone pattern[19] (Figure 1: A) and the packing does not reveal significant intermolecular interactions; the shortest distance determined for C(H)···O of 346 pm and for C(H)···N of 339 pm with an angle of 136° are both outside the range of effective hydrogen bonds[20][21].

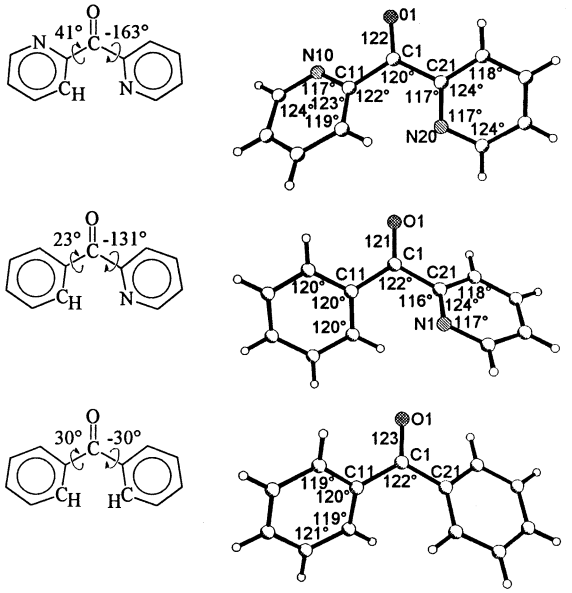
In the molecular structure, which lacks any symmetry, the planar pyridine rings are twisted differently around the planar ketone subunit C11−C(O)−C21 by torsional angles ω(C1−C11−N10) = 41° for ring I and ω(O1−C1−C21−N20) = −163° for ring II (5: ⊘: N, ⊛: O, ○: C, o: H).



(5)

The planes of rings I and II are twisted relative to each other by 56° and their N centers approach an *anti* configuration, which avoids repulsive interaction between the nitrogen N20 electron pair and the in-plane electron density around the center O1. In contrast, the N10 electron pair interacts more strongly, as indicated by the considerably larger twisting angle ω(O1−C2−C11−N10) = 41°, which may even be limited by the often unfavorable lattice packing for twisted molecules with close-to-perpendicular halves.

A structural comparison of di(2-pyridyl) ketone with the isoelectronic molecules phenyl 2-pyridyl ketone[1] and benzophenone[2] provides additional information (6). Both compounds crystallize in the orthorhombic space group $P2_12_12_1$ with $Z = 4$ molecules in the unit cell.



(6)

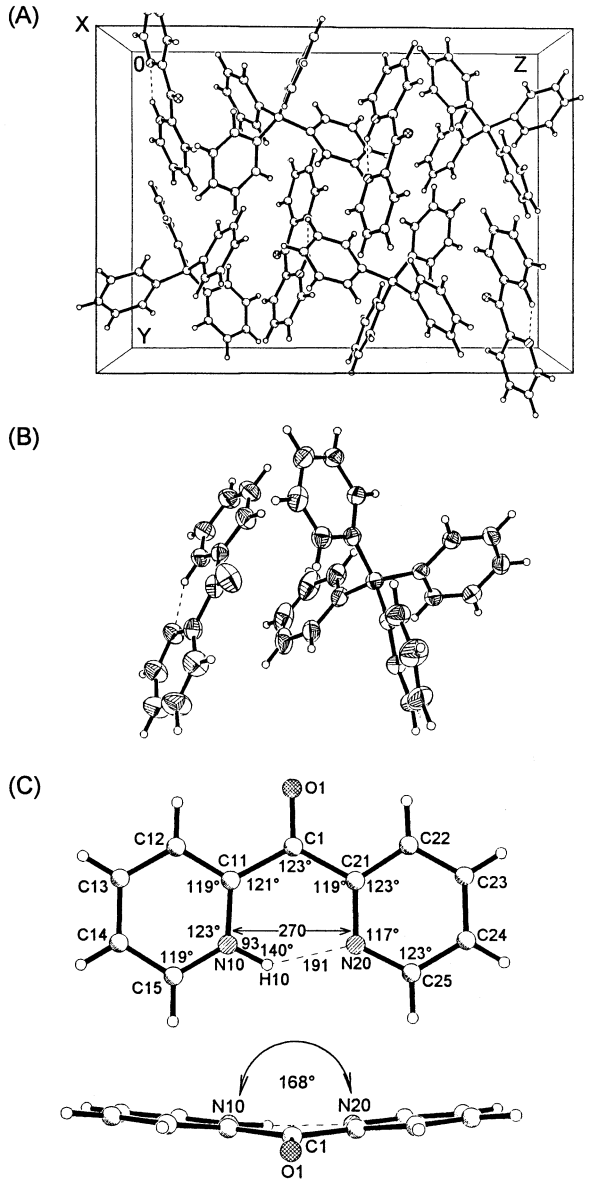
Benzophenone exhibits C_2 symmetry due to the opposite torsion of its phenyl groups by ω(OC−CC) = ±30°; which minimizes the spatial repulsion between the hydrogens at centers C12 and C22. Smaller structural differences between the iso(valence)electronic molecules (Eq. 6) concern predominantly the angles around the ring carbonyl and aza-substitution centers. Most eye-catching is the observation that on increasing substituent exchange, 2-pyridyl → phenyl, the relative twisting of the two six-membered, iso(valence)electronic rings decreases from Δω = 122° in di(2-pyridyl) ketone via 108° in phenyl (2-pyridyl) ketone to 60° in benzophenone (6).

2-Pyridinio 2-Pyridyl Ketone Tetraphenylborate

The tetraphenylborate salt crystallizes as yellow blocks from acetone solution on covering it with an *n*-hexane layer (Experimental Section). The crystals are monoclinic ($P2_1/n$) and contain $Z = 4$ formula equivalents in the unit cell (Figure 2: A).

The bulky tetraphenylborate anion prevents intramolecular contacts. The structure of the protonated molecular cation can be characterized by its intramolecular hydrogen bond $^+N-H\cdots N$ (Figure 2: C) with a distance $N^+\cdots N$ of 270 pm and an angle ∢ N−H−N of 140°, which therefore should be considerably weaker than the prototype ones of 253 pm length in protonated tetra(2-pyridyl)pyrazine[20].

Figure 2. Crystal structure of 2-pyridinio 2-pyridyl ketone tetraphenylborate at 200 K: (A) Unit cell (monoclinic $P2_1/n$, $Z = 4$) in x direction, (B) salt structure (50% thermal ellipsoids) and (C) molecular cation with intramolecular hydrogen bond $^+N-H\cdots N$ in top view with structural data and center numbering (o: ⊘: N, ◉: O, ○: C, H) as well as in side view



The molecular cation is bent by about 12° along the bond C1−O1, which is shifted out of each of the ring planes by 10°. The planar pyridine rings are not twisted relative to each other, in contrast to the angle of 8° between the planes found in the tetrafluoroborate[11]. One pyridine *ipso* angle ◁ C−N−C is widened by protonation from 117° to 123°[23] and the adjacent angles show opposite behavior (Figure 2: C). The carbonyl group angle ◁ C11−C1−C21 of 123° is widened from 120° in di(2-pyridyl) ketone (6), presumably due to the 270 pm long hydrogen bond $N^+-H\cdots N$ (Figure 2: C).

The protonation of di(2-pyridyl)amine generates the same hydrogen-bonding pattern and the six-membered rings become planar. In addition to the tetraphenylborate (Figure 2), the chloride hydrate (Figure 3), tetrafluoroborate[11], also the squarate and analogous salts of di(2-pyrimidyl)amine have been structurally characterized[24].

Table 1. Selected bond lengths [pm] and angles [°] of 2-pyridinio 2-pyridyl ketone tetraphenylborate (numbering of centers Figure 2: B)

O(1)−C(1)	121.3(2)	N(20)−C(21)	134.5(2)
C(1)−C(21)	149.0(2)	C(21)−C(22)	137.4(2)
C(1)−C(11)	150.2(2)	C(22)−C(23)	137.2(3)
N(10)−C(15)	133.2(2)	C(23)−C(24)	137.2(3)
N(10)−C(11)	135.4(2)	C(24)−C(25)	138.0(3)
C(11)−C(12)	137.2(2)	C(32)−C(33)	139.3(2)
C(12)−C(13)	138.3(3)	N10···N20	269.8(2)
C(13)−C(14)	137.6(3)	N10−H10	93(2)
C(14)−C(15)	137.3(2)	N20···H10	191(2)
N(20)−C(25)	133.2(2)		
O(1)−C(1)−C(21)	119.9(2)	N(10)−C(15)−C(14)	119.4(2)
O(1)−C(1)−C(11)	117.2(2)	C(25)−N(20)−C(21)	117.0(4)
C(21)−C(1)−C(11)	122.9(1)	N(20)−C(21)−C(22)	123.2(2)
C(15)−N(10)−C(11)	122.9(2)	N(20)−C(21)−C(1)	118.6(1)
N(10)−C(11)−C(12)	118.9(2)	C(22)−C(21)−C(1)	118.3(1)
N(10)−C(11)−C(1)	120.7(4)	C(23)−C(22)−C(21)	118.6(2)
C(12)−C(11)−C(1)	120.4(4)	C(24)−C(23)−C(22)	119.3(2)
C(11)−C(12)−C(13)	119.5(2)	C(23)−C(24)−C(25)	118.5(2)
C(14)−C(13)−C(12)	119.8(2)	N(20)−C(25)−C(24)	123.4(2)
C(15)−C(14)−C(13)	119.5(2)	N(10)−H(10)···N(20)	140(2)

Dihydroxydi(2-pyridinio)methane Dichloride Monohydrate

The light-yellow salt, prepared from di(2-pyridyl) ketone and hydrochloric acid in water, crystallises from acetone solution as yellow-orange needles (Experimental Section). In the monoclinic unit cell of space group $C2/c$ with $Z = 4$ formula equivalents, the cation is arranged on a twofold axis with centers C1 and O1 on special positions. The asymmetric unit therefore corresponds to half a formula unit (Figure 3).

The structural analysis confirms a twofold protonation and hydration of the keto group to the geminal diol, $>C=O + H_2O \rightarrow >C(OH)_2$, which forms a dichloride dianion [$^-Cl\cdots HOH\cdots Cl^-$] via hydrogen bonds (C)O−H···Cl^- and $Cl^-\cdots HO(H)$ (Figure 3: B and C). The individual hydrogen-bonded aggregates are connected by additional bridges $^+N-H\cdots Cl^-$ to form polymeric sheets with alternating units along the z direction (Figure 3: A).

The symmetry-equivalent hydroxy groups (7: transformation of equivalent positions: $-x + 1$, $-y + 1$, $-z + 3$) bridge the two chloride anions with distances O(H)···Cl^- of 304 pm and an angle ◁ O−H···Cl^- of 175°. In addition, the two Cl^- anions are bridged by one water molecule with distances O(H)···Cl^- of 322 pm and angles ◁ O(H)···Cl^- of 174° (Figure 3: C and Table 2). The protonated pyridinium centers form additional hydrogen bonds $^+N-H\cdots Cl^-$ to another two Cl^- anions with distances N10···C11 of 307 pm and angles ◁ $^+$N(H)···Cl^- of 163° (7). In the doubly protonated dication with an almost tetrahedral central carbon atom, the pyridine rings are twisted each by 85° relative to the angle-halving line O2−C1−O2′ (7). The planar pyridinium rings have standard bond lengths C−C of 138 pm and C−N of 134 pm (Table 2).

Figure 3. Crystal structure of dihydroxydi(2-pyridinio)methane dichloride monohydrate at 200 K: (A) Unit cell (monoclinic; *C*2/*c*, $Z = 4$) in x direction, (B) dication complex (50% thermal ellipsoids) with numbering and (C) hydrogen-bond network (▨: N, ▩: F, ●: O, ○: C, o: H)

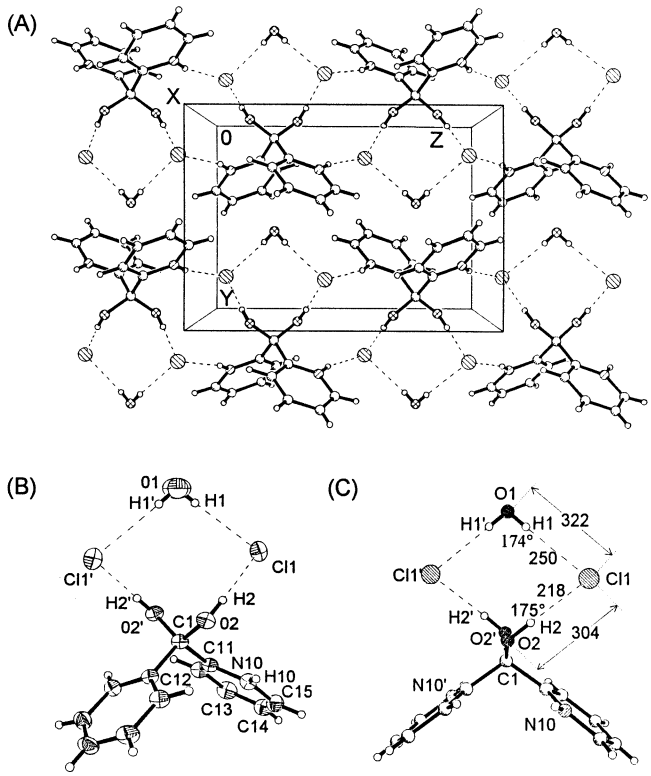
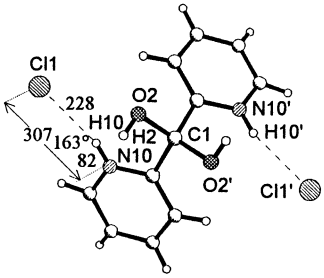


Table 2. Selected bond lengths [pm] and angles [°] of dihydroxydi(2-pyridinio)methane dichloride monohydrate including the structural data for the hydrogen bonds (numbering of centers Figure 3: C)

Bond lengths			
O(2)−C(1)	138.9(1)	N(10)−C(15)	134.0(2)
C(1)−C(11)	153.0(2)	C(11)−C(12)	138.0(2)
C(1)−O(2A)	138.9(1)	C(12)−C(13)	138.3(2)
C(1)−C(11A)	153.0(2)	C(13)−C(14)	138.3(3)
N(10)−C(11)	134.4(2)	C(14)−C(15)	138.1(2)
Bond angles			
O(2)−C(1)−C(11)	110.9(1)	C(1)−C(11)−N(10)	116.2(1)
O(2)−C(1)−O(2A)	114.1(2)	C(1)−C(11)−C(12)	124.6(1)
C(11)−C(1)−O(2A)	106.4(1)	N(10)−C(11)−C(12)	119.2(1)
O(2)−C(1)−C(11A)	106.4(1)	C(11)−C(12)−C(13)	119.1(1)
C(11)−C(1)−C(11A)	108.1(2)	C(12)−C(13)−C(14)	120.4(1)
O(2A)−C(1)−C(11A)	110.9(1)	C(13)−C(14)−C(15)	118.8(2)
C(11)−N(10)−C(15)	123.0(1)	N(10)−C(15)−C(14)	119.5(2)
Hydrogen bonds			
N10−H10···Cl1			
N10···Cl1 307	H10···Cl 228	N10−H10 82	
O1−H1···Cl1			
O1···Cl1 322	H1···Cl 250	O1−H1 73	
O2−H2···Cl1′			
O2···Cl1 304	H2···Cl1 218	O2−H2 86	
N10−H10···Cl1163	O1−H1···Cl1 174	O2−H2···Cl1′ 175	

Structural Changes on Single and Double Protonation of Di(2-pyridyl) Ketone

The precursor molecule $(H_5NC_6)_2C{=}O$ is intricately twisted as a result of its three lone pairs ($2n_N^{\sigma} + 1n_O^{\sigma}$)



and shows tremendous structural differences on single and double protonation to salts containing the anion $[B(C_6H_5)_4]^-$, which cannot be protonated, and the hydrogen-bond acceptor Cl^- (1 and Figures 1 to 3).

In the monocation, generated in acetic acid by the addition of sodium tetraphenylborate (Figure 2), the pyridine rings of di(2-pyridyl) ketone (Figure 1) are planarized by the formation of an intermolecular hydrogen bond. In contrast, aqueous hydrogen chloride produces a dication with both nitrogen centers protonated and the resulting hydrate embedded in a complex hydrogen-bond network (Figure 3). Extensive quantum-chemical calculations based on the experimental structural data allow to rationalize the results.

Approximate PM3 Enthalpy Hypersurface for Di(2-pyridyl) Ketone

For the calculations of the 22-center/68-electron molecule, which were performed with the aim of excluding crystal-packing effects, the semiempirical PM3 procedure[25] has been choosen despite some reservations concerning the correct prediction of finer details[26]. Within the energetic hierarchy of structural changes[27], rotations around bonds that are sterically not too overcrowded frequently require the lowest activation enthalpy and, accordingly, for the molecule with $n = 22$ centers and $3n - 6 = 60$ degrees of freedom, the two ring-torsion modes have been selected. Variation of the angles in 10° steps followed by optimization of each geometry generated using the PM3 Fletcher−Powell subroutine (Experimental Section) produced an enthalpy-of-formation grid, which was interpolated to yield the hypersurfaces (Figure 4).

The PM3 hypersurface calculation is based on the experimentally determined structural coordinates[2] (Figure 1) with the two pyridine rings rotated independently by $\Delta\tau_1$ or $\Delta\tau_2$ (9). As expected, the resulting enthalpy hypersurface for di(2-pyridyl) ketone (Figure 4) exhibits mirror symmetry for $\Delta\tau_2$ at $\tau_1 = 0°$ or 180°.

The hypersurface is best rationalized starting from the experimental (Figure 4: ■) and calculated minima (Figure 4: □) together with the 6 saddle points generated by the independent rotations $\Delta\tau_1$ and $\Delta\tau_2$ (Figure 4: □). Of these saddle points, $\tau_1 = 0°/\tau_2 = 90°$ and $\tau_1 = 90°/\tau_2 = 0°$ are connected by a twofold rotation axis and $\tau_1 = 90°/\tau_2 = 0°$ and $\tau_1 = 270°/\tau_2 = 0°$ by a mirror plane ($\tau_1 = 180°/\tau_2 = 0°$ to 0°), whereas $\tau_1 = 90°/\tau_2 = 90°$ as well as $\tau_1 = 90°/\tau_2 = -90°$ are located between the maxima ◫ and ▩ (Figure 4).

The crystal structure determined (Figure 4: ■) has torsion angles $\tau_1 = 41°$ and $\tau_2 = -163°$ and its enthalpy of

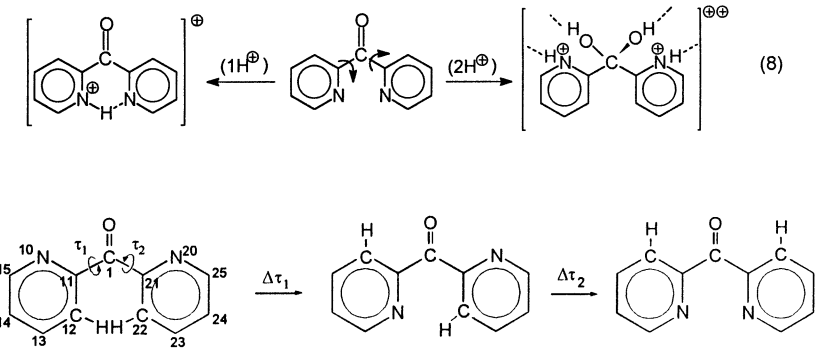
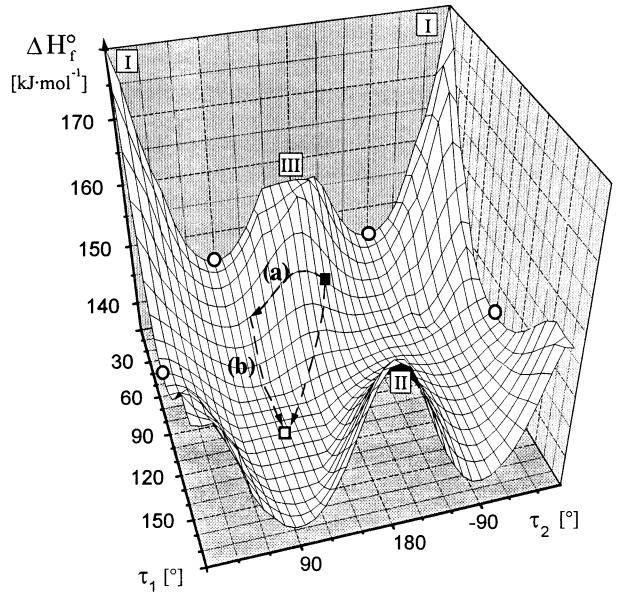


Figure 4. PM3 enthalpy of formation hypersurface for independent rotation of both pyridine rings in di(2-pyridyl) ketone around the torsion angles τ_1 and τ_2 (turning at $\tau_1 = \tau_2 = 180°$ by 180° provides the other mirror halve with ■ crystal structure, □ PM3 minimum, ◫ to ▥ PM3 maxima, ○ saddle points and (a), (b) cuts discussed in text



formation is calculated after PM3 geometry optimization of all additional centers to be $\Delta H_f° = +145$ kJmol^{-1} (cf. Experimental Section; with distance corrections up to ±2 pm and angle changes up to ±3°). The minimum of the PM3 enthalpy hypersurface [Figure 4: □ and (8)] at $\tau_1 = 110°$ and $\tau_2 = 103°$, is predicted to be +133 kJmol^{-1}. No rotational barrier exists between the crystal structure (Figure 4: ■) and the PM3-optimized enthalpy minimum (Figure 4: □)[2]. For the two possible planarizations to conformations with $\tau_1 = 0$ and $\tau_2 = 0°$ or 180° (Figure 4: ◫ and ▥), enthalpy differences $\Delta\Delta H_f° = 47$ or 27 kJ mol^{-1} were calculated relative to the twisted PM3 minimum (Figure 4: □).

For rationalization of the repulsion CH···HC in the calculated planar confirmation ◫, the C···C distance of only 320 pm is well within the sum of two CH_3 van der Waals radii of 400 pm[23], and the lone-pair interaction N···N in ▥ at a separation of 275 pm is also within the sum of two nitrogen van der Waals radii of 300 pm.

In the nitrogen-free parent benzophenone (6) both rings are twisted by 30° because no CH···N interactions exist as, for instance, in the saddle-point conformation (Figure 4: □). For the mono(2-pyridyl)-substituted phenyl ketone (6), a structure with torsion angles $\tau_1 = 23°$ and $\tau_2 = -131°$ was determined[1] and an optimized PM3 enthalpy of formation $\Delta H_f° = 109$ kJmol^{-1} predicted for torsion angles $\tau_1 = 119°$ and $\tau_2 = 117°$.

To summarize, the PM3 enthalpy hypersurface calculations (Figure 4) suggest that di(2-pyridyl) ketone should exhibit twisted rings in both the gas and crystalline phases. The crystal-packing effects on the molecular conformation are thus, at best, only small.

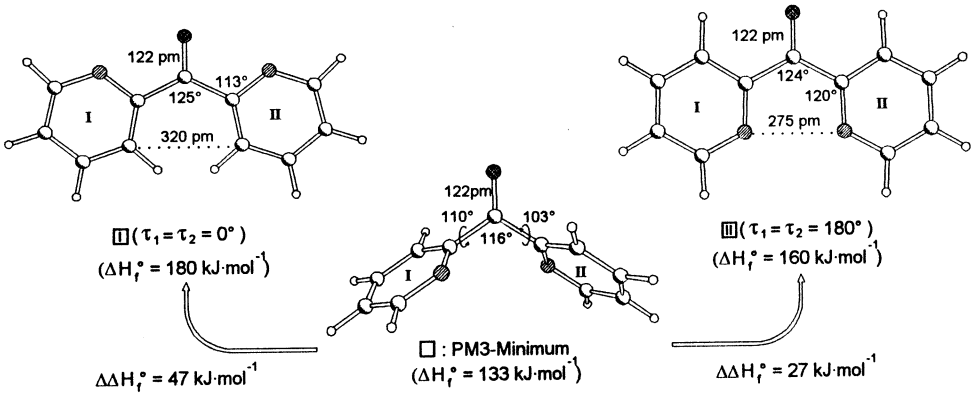
2-Pyridinio 2-Pyridyl Ketone Tetraphenylborate − Hydrogen-Bond Enthalpy and PM3 Charge Distribution

The crystal structure of the monoprotonated di(2-pyridyl) ketone cation (Figure 2 and Table 1) is satisfactorily reproduced by geometry-optimized PM3 calculations (11: A).

A coplanar conformation is predicted for the pyridine rings and a N−N distance of 260 pm is calculated for the intramolecular hydrogen bond $^+$N−H···N. Its bond enthalpy can be approximated by an enforced rotation ω(OC1−CN) = 180° of pyridine ring I according to $\Delta\Delta H_f°(N^+-H\cdots N) = \Delta H_f°(\omega = 0°; 180°) - \Delta H_f°(\omega = 180°; 180°) = (777 - 756)$ kJmol^{-1} = 21 kJmol^{-1}, which would be within the usual range for cationic hydrogen bonds $^+$N−H···N[20][23].

Dihydroxydi(2-pyridinio)methane Dichloride Monohydrate

Di(2-pyridyl) ketone remains largely unhydrated in aqueous solution (Eq. 3) and exists as the ketone tautomer[6][28]. On addition of aqueous HCl, however, both pyridine substituents are protonated and the keto group is hydrated to the geminal diol (Eq. 3).The crystal structure is dominated by three different hydrogen bonds to chloride anions, which are excellent hydrogen-bond acceptors[19][29][30]. The protonated pyridine substituents form bridges $^+$N−H···Cl with distances $^+$N···Cl$^-$ of 307 pm (Figure 3: C) and the hydroxy substituents of the diol >C(OH)$_2$ two bridges O−H···Cl$^-$



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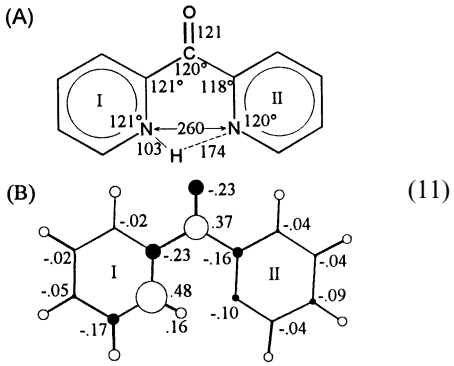

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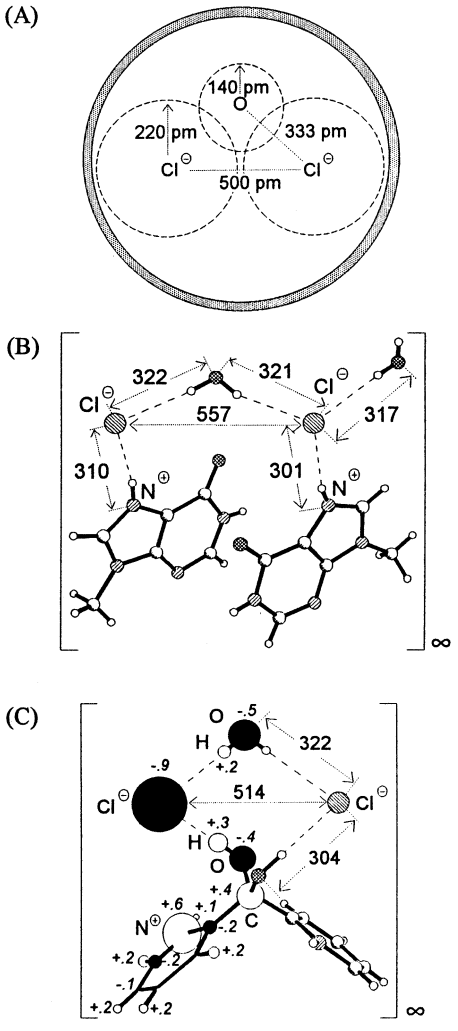

(12)

with a O···Cl^- distance of 304 pm. The additional water molecule connects two adjacent chloride anions by bridges Cl^-···HOH···Cl^- with distances Cl^-···O of 322 pm. Hundreds of these dichloride hydrate fragments are registered in the Cambridge Structural Database and in well over 30 of them, the distance Cl^-···Cl^- is below 500 pm[30]. In general, a cavity within the crystal (Eq. 12: A) containing two spatially accessible proton acceptors such as energetically favourable Cl^- anions, can advantageously be filled with water in accord with the van der Waals radii, r_{Cl^-} = 220 pm and r_O = 140 pm. Two characteristic examples[24][29][30] show that the intermolecular water-bridging of heterocyclic salts occurs at a Cl^-···Cl^- distance of 557 pm (12: B). The shorter Cl^-···Cl^- distance of 514 pm (12: C) in our intramolecular dichloride hydrate Cl^-···HOH···Cl^- results from hydrogen bonding by geminal hydroxy groups of the dipyridinio ketone hydrate, which is formed from di(2-pyridyl) ketone in aqueous HCl (3).

Starting from the crystal-structure data, PM3 calculations have been performed to approximate the hydration enthalpy of the dipyridinio ketone dichloride hydrate fragment, $\Delta\Delta H_{hydr} \approx \Delta\Delta H_f°$, and its enthalpy of formation difference to the independently calculated value for the aggregate (12: C). The resulting value ΔH_{hydr} of about 10 kJmol^{-1} indicates two rather weak Cl^-···(H)O bridges[19][29] stengthened by a cooperative effect[34]. In addition, PM3 charge densities have been obtained (12: C, left hand side). For the positive charge in the pyridinium rings, dominant $N^{\delta+}$ localization together with some transfer to the ketone carbon center are predicted, increasing the diol acidity. The negative charge remains largely on the chloride anions as well as to a smaller extent at the oxygen centers. The positive charges at the bridging hydrogens indicate that the quadrangle of four Cl^-···(H)O bonds in the 10-membered ring must considerably reduce the repulsion Cl^-···Cl^- between the two negatively charged chloride centers at a distance of only 514 pm.

Conclusions

The protonation of di(2-pyridyl) ketone by different acid systems and the subsequent crystallization with various

counter anions provides another example from our group[24][34] of how diverse the results can be (cf. Eqs. 3 and 4). With the tetraphenylborate counter anion, an intramolecular protonation at a pyridine N center takes place and a $N^+(H)\cdots N$ hydrogen bond planarizes the severely twisted molecule (Figure 2). The stronger acid HCl protonates twice and the addition of water transforms the ketone into its hydrate, an optimal ligand for the complexation of two Cl^- anions. The salt crystallizes as a polymeric dihydroxydi(2-pyridinio)methane dichloride monohydrate (Figure 3) containing a stabilizing $Cl^-\cdots HOH\cdots Cl^-$ link. The effect is already well-documented in the Cambridge Structural Database and to relieve some of the negative charge repulsion $Cl^-<\cdots>Cl^-$ between the adjacent anions at relativelys short distance.

There are numerous reports in the literature[19][27][29] of how small changes in crystallisation conditions can cause drastic differences in the molecular crystals grown. The twofold protonated and, in addition, hydrated salt of the di(2-pyridyl) ketone obtained from aqueous hydrochloric acid solution is another exemplary case which provides some insight into the complex network of protonation, solvation or association equilibria which often precede crystallization.

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Experimental Section

Di(2-pyridyl) Ketone: Di(2-pyridyl) ketone is commercially available (Aldrich, 12,722-1, mp. 53−55°C). Its UV spectrum in *n*-hexane shows adsorption maxima at 43300; 37900, and 28000 cm^{-1} (ref.[24]: 42600 and 37300 cm^{-1}). Single crystals were grown by slow evaporation of a solution of 100 mg in 2 ml of benzene; crystal structure determination cf. ref.[1].

2-Pyridinio 2-Pyridyl Ketone Tetraphenylborate: To a solution of 500 mg of di(2-pyridyl) ketone in 10 ml of 2.5% acetic acid under stirring a solution of 1.25 g of sodium tetraphenylborate in 10 ml of water was added. The yellow, voluminous deposit was suction-filtered, washed three times with water and dried at 10^{-2} mbar; m.p 128°C. − $C_{35}H_{29}BN_2O$ (504.4): calcd. C 83.34, H 5.79, N 5.55; found C 83.81, H 5.88, N 5.43. Single crystals were grown from a solution of 30 mg of 2-pyridinio 2-pyridyl ketone tetraphenylborate in 1 ml of acetone by adding a layer of *n*-hexane; after 4 h yellow blocks have crystallized.

Crystal Structure Determination: $C_{35}H_{29}BN_2O$, monoclinic, space group $P2_1/n$, a = 9.816(1), b = 14.299(1), c = 19.613(1) Å, β = 91.64(1)°, U = 2751.7(4) Å^3, Z = 4, $D_{calcd.}$ = 1.218 g cm^{-3}, $F(000)$ = 1064, μ = 0.07 mm^{-1}, Mo-K_α (λ_α = 0.71073 Å). T = 200 K, θ-2θ scan, 3° ≤ 2θ ≤ 53° on a Siemens P4 diffractometer. Reflections measured = 7153; independent reflections = 5653; data used for refinement = 4064; parameters = 362. The structure was solved by direct methods and refined on F^2 using SHELXL 93. R = 0.0434 ($wR2$ = 0.0963) for $I < 2\sigma(I)$ and Goof = 1.025. Further details of the crystal-structure investigations may be obtained from the Fachinformationszentrum Karslruhe, D-76344 Eggenstein-Leopoldshafen (Germany), on quoting the depository number CSD-407078.

Dihydroxydi(2-pyridinio)methane Dichloride Monohydrate: A solution of 500 mg (2.71 mmol) of di(2-pyridyl) ketone in 25 ml of aqueous 0.2 M HCl was stirred for 1 h at room temperature. Water evaporation at 10^{-1} mbar and 6 h of drying at 10^{-2} mbar yielded the light-yellow chloride salt with m.p. 102°C. − $C_{11}H_{14}Cl_2N_2O_3$ (293.1): calcd. C 45.08, H 4.81, N 9.56; found C 44.55, H. 4.72, N 9.51. Single crystals were grown by slow evaporation of a solution containing 50 mg of dihydroxydi(2-pyridinio)methane dichloride monohydrate in 3 ml of acetone. After 1 d, yellow-orange needles crystallized.

Crystal Structure Determination: $C_{11}H_{14}Cl_2N_2O_3$, monoclinic, space group $C2/c$, a = 13.384(1), b = 8.432(1), c = 11.865(1) Å, β = 90.93(1)°, V = 1338.8(2) Å^3, Z = 4, $D_{calcd.}$ = 1.454 g cm^{-3}, $F(000)$ = 608, μ = 0.49 mm^{-1}, Mo-K_α (λ_α = 0.71073 Å). T = 200 K, ω-θ scan, 3° ≤ 2θ ≤ 65° on a Siemens P4 diffractometer. Reflections measured = 2623; independent reflections = 2386; data used for refinement = 1877; parameters = 111. The structure was solved by direct methods and refined using SHELXLS for R = 0.0395 (Rw = 0.0381) for $I < 2\sigma(I)$ and Gof = 1.8880. Further details of the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), on quoting the depository number CSD-407077.

PM3 Calculations[25]: Performed using the MOPAC/SCAMP IV/1 program package (Dr. T. Clark, University of Erlangen) on the IBM RISC 6000-320 of our group. For the hypersurface approximation, the starting points were the structural coordinates, and the rotational barriers were calculated in 10° steps with each total geometry optimization using the PM3 Fletcher−Powell subroutine. The resulting enthalpy of formation grid was graphically interpolated to produce the hypersurfaces presented.

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