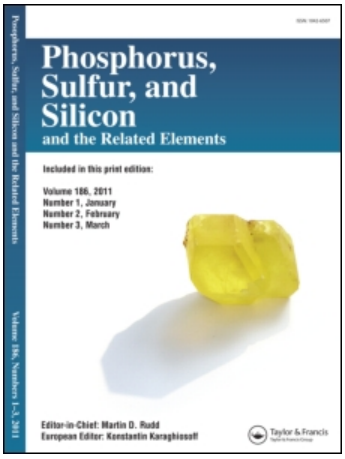

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Novel Hydrogen-Bridged Molecular Aggregates: Design, Structures and Potential Calculations

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NOVEL HYDROGEN-BRIDGED MOLECULAR AGGREGATES: DESIGN, STRUCTURES AND POTENTIAL CALCULATIONS

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Abstract: Despite of well over 10000 entries in the Cambridge Structural Data Base, still numerous novel aspects of hydrogen bonding in single crystals are discovered. Topics reported comprise: (i) the use of non-protonable anions to prepare prototype salts with $NH^{\oplus}N$ bridges, partly accompanied by both structure and color changes (chemical mimesis), (ii) cooperative effects in H-bridged dimers and polymers, (iii) the shortest hydrocarbon to oxygen bridge reported so far in $(O_2N)_3CH\cdots OR_2$, (iv) triclinic and orthorhombic polymorphs of dipyridylamine dimers or isomorphic crystals of ditosyl-p-phenylenediamine, which due to an H bridge enforced packing motif contain within identical unit cells solvent molecules as different as acetone or tetrahydrofurane, (v) chloride hydrates in single crystal lattice cavities of nitrogen heterocycles. All structures determined are rationalized by extensive energy hypersurface calculations.

THE MOLECULAR STATE APPROACH TO DESIGN CRYSTALS OF ORGANIC COMPOUNDS

Within the time domain of dynamic relaxation, the structure of a molecule can change considerably with its energy and, above all, with the number of its electrons.[1,2] Charges, generated by redox reactions, often inflict severe distortions such as the twisting of the molecular halves in ethylene dianions and dications around the central CC axis, which simultaneously stretches from a C=C double to a C-C single bond[2] (Figure 1). All of these structural changes - including also those due to spatial overcrowding[2] within molecules such as triisopropylamine with its flattened NC_3 skeleton (Figure 1) - nowadays can be predicted either from relevant molecular state measurement data or by approximate energy hypersurface calculations, thereby increasing the hit rate of targeted synthesis efforts and consecutive, often laborious attempts to grow single crystals from aprotic solutions ($c_{H\oplus} < 1$ ppm) under argon.[2]

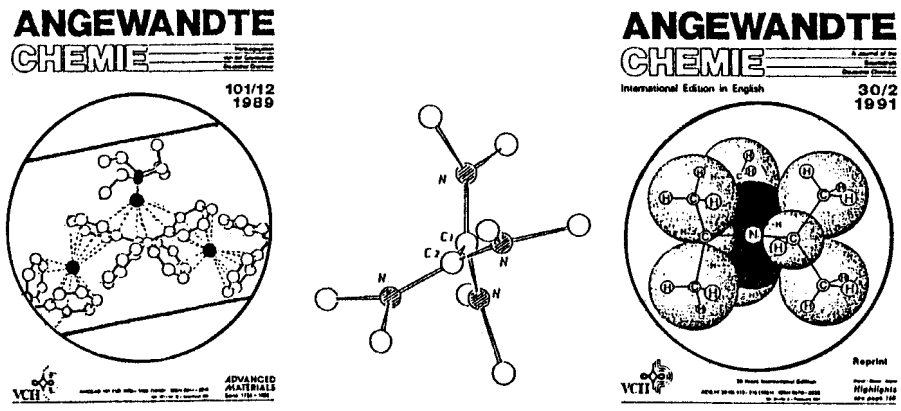


FIGURE 1. Structural distortion of tetraphenylethylene on reduction to its solvent-shared contact triple dianion[3] as well as of tetrakis(dimethylamino)ethylene on oxidation to its dication[3] and flattening of the NC_3 skeleton of triisopropylamine due to steric congestion.[4]

Altogether, molecular crystals contain organic compounds in their respective ground state close to or even in their global energy minima and with largely "frozen" molecular dynamics.[2,5,6] An analysis of crystal lattices, therefore, not only provides an advantageous starting point for the discussion of numerous molecular properties and their quantum chemical calculation, but moreover can yield some static aspects of molecular self-organization.[5,6] Of these, in addition to cation solvation[2,5-7] and to van der Waals interactions in sterically overcrowded organosilicon compounds,[5,6,8,9] specific H bridge effects have been investigated by the Frankfurt group since 1992.[2] Our studies comprise both new preparative methods, aimed especially at hitherto unknown hydrogen bridged molecular aggregates as well as potential calculations, predominantly to evaluate cooperative effects.

CHEMICAL MIMESIS OF DIPROTONATED TETRAPYRIDINEPYRAZINE AND OTHER INTRAMOLECULAR H-BRIDGES ENFORCED BY A NON-PROTONABLE COUNTERANION

Our first contribution to hydrogen bonding phenomena reported on the "chemical mimesis" (safety attire of animals to adapt in color and/or shape to their environment) of tetra(2-pyridine)pyrazine dication on replacement of the

topotactive $H^{\oplus}$bridge acceptors $Cl^{\ominus}$ by non-protonable tetraphenyl borate anions (Figure 2).

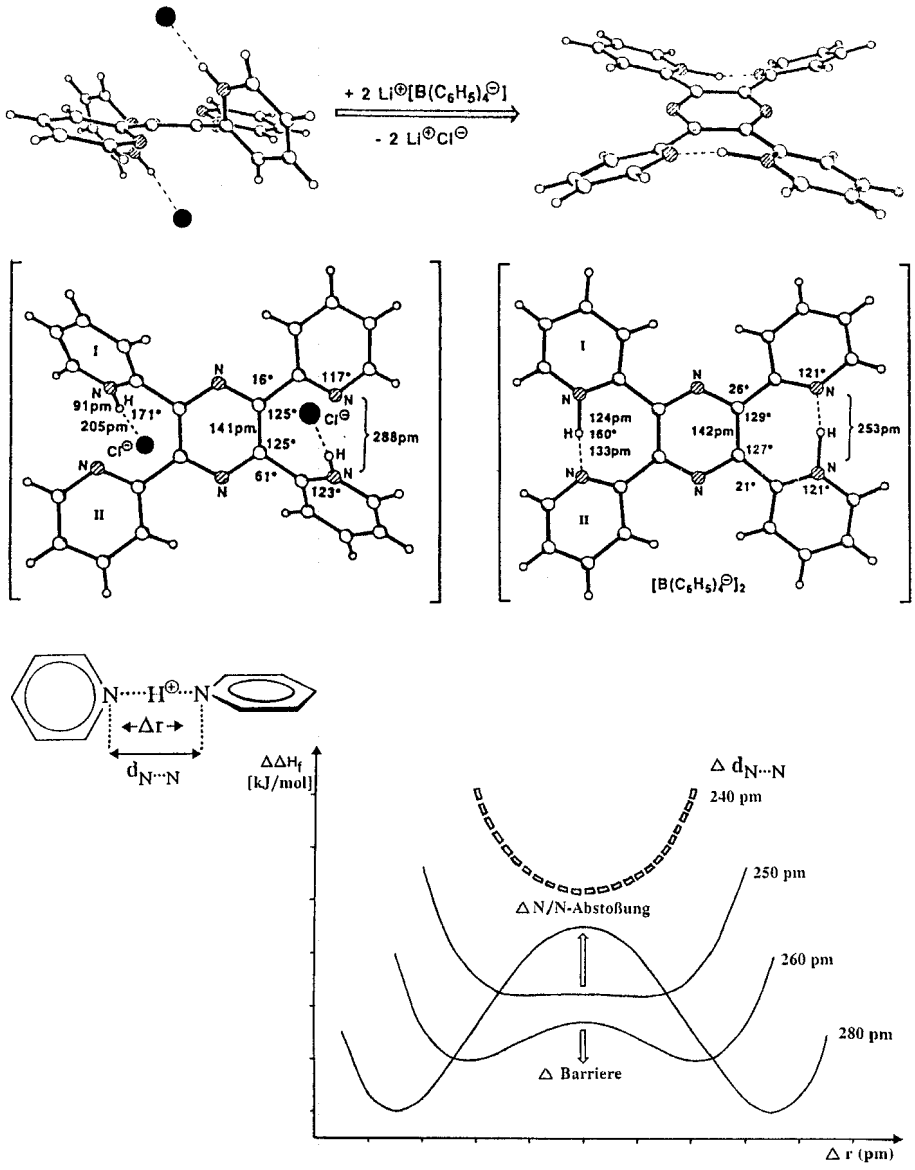


FIGURE 2. Structures of diprotonated tetra(2-pyridine)pyrazine salts with chloride and non-protonable tetraphenylborate anions as well as semiempirical potentials curves for pyridinium pyridine, the H-bridged subunit.[9]

On intramolecular H bridge flattening, the dication turns yellow. To rationalize the extremely short and almost symmetric N···H···N bond, distance-dependent potential calculations have been performed based on the known neutron diffraction data of pyridiniumpyridine perchlorate:[9] for its N···N distance of 270 pm a double minimum results, whereas for the 253 pm determined in the twofold H-bridged tetra(2-pyridine)pyrazine an almost single minimum potential is predicted, within which the proton at room temperature should oscillate with a frequency of about 10^{-9} sec.

The formation of other novel $H^{\oplus}$-bonded molecular aggregates such as quinuclidinium quinuclidine can be enforced analogously by recrystallizing a mixture the respective trialkylammonium hydrochloride, lithium tetraphenylborate and the corresponding trialkylamine from a solution in acetone or ethanol[10] (Figure 3).

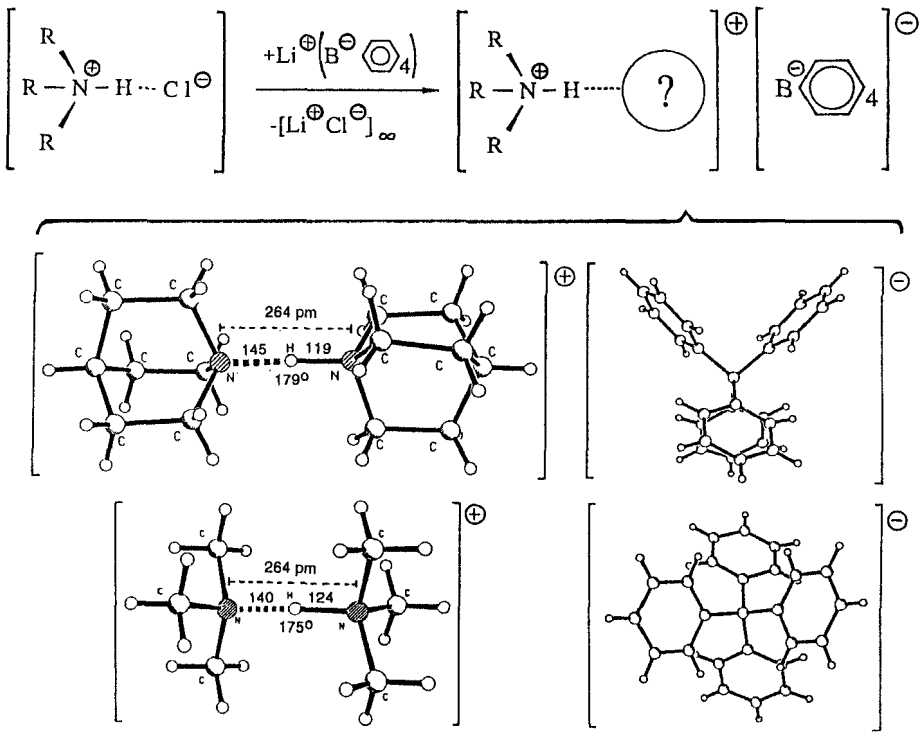
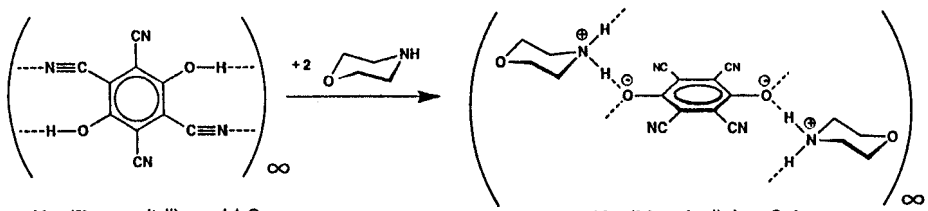


FIGURE 3. H-Bridge design by use of an unprotonable anion to enforce specific connectivities and single crystal structures (200 K) of quinuclidinium quinuclidine and of trimethylammonium trimethylamine tetraphenylborates.

Trimethylammonium trimethylamine tetraphenylborate $[(H_3C)_3N^{\oplus}H\cdots N(CH_3)_3][B^{\ominus}(C_6H_5)_4]$ could be crystallized as well (Figure 3) and exhibits the same $N(H^{\oplus})N$ distance of 264 pm. Altogether, the use of non-protonable counter anions $[ER_n^{\ominus}]$ with delocalized and/or sterically shielded negative charge, which favors external hydrogen bonds of a molecule $M^{\oplus}H\cdots X$ over intramolecular ones, $[MH^{\oplus}][ER_n^{\ominus}]_m$ (Figure 2) or $[M^{\oplus}H\cdots M][ER_n^{\ominus}]$ (Figure 3), allows to design hitherto inaccessible H-bridged molecular aggregates.[9,10]

H DONOR/ACCEPTOR BONDS AND COOPERATIVE EFFECTS

Hydrogen bonding depends, as demonstrated (Figure 2), on the relative H donor and H acceptor properties of the centers involved. Another illustrative example is the tetracyanohydroquinone polymer with $(OH\cdots NC)_2$ double bridges, which can be converted with considerable structural reorganization into a $(O^{\ominus}\cdots H^{\oplus}NC)$ charge-polarized one by recrystallization in the presence of morpholine, a base stronger by 20 orders of magnitude:[11]



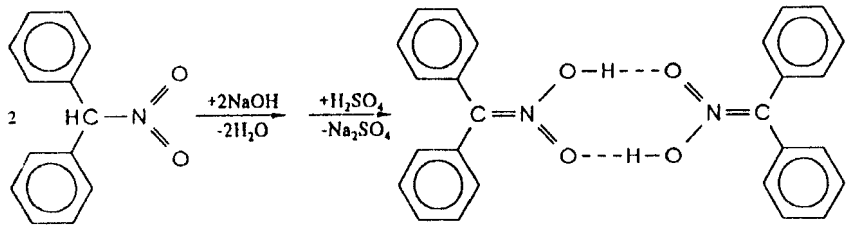
pK_B (Benzonitril) = -11.0 ---------- pK_B (Morpholin) = 8.4

$\Delta pK_B \approx 19.4$ (1)

In addition, the structural data for the tetracyanohydroquinone dianion demonstrate how well its negative charges are delocalized.

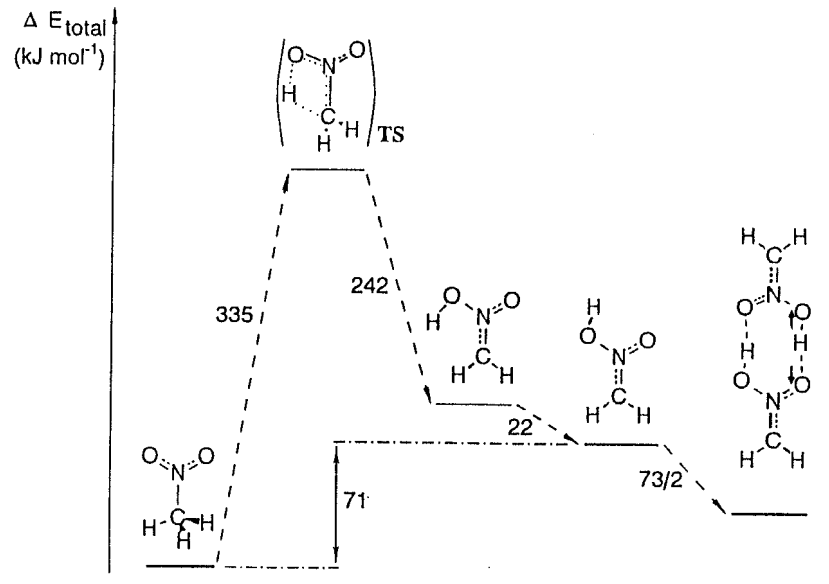
Extensive quantum chemical model calculations have been performed to evaluate the cooperative effects in both H-bonded polymers (2): For tetracyanohydroquinone, an increase of approximately 10 % is predicted within a $(OH\cdots NC)_2$ double bridge pair relative to two $(OH\cdots NC)_1$ single interactions.[9] In the morpholinium salt, however, due to the additional Coulombic interactions, an increase of the cooperative effect by about 32 % is calculated.

Cooperative effects have been investigated repeatedly by the Frankfurt Group: Our largest difference between monomeric and dimeric H bridges $(E\cdots H\cdots E)_{n=1,2}$ predicted so far by PM3 calculations based on structural data is about 40 % in the novel aci-diphenylnitromethane dimer:[12]



(2)

An ab initio total energy profile for the parent molecule nitromethane with its extremely high tautomerisation barrier allows to rationalize in addition, why aci-nitro compounds usually have to be prepared by acidification of their nitronate salts (2).

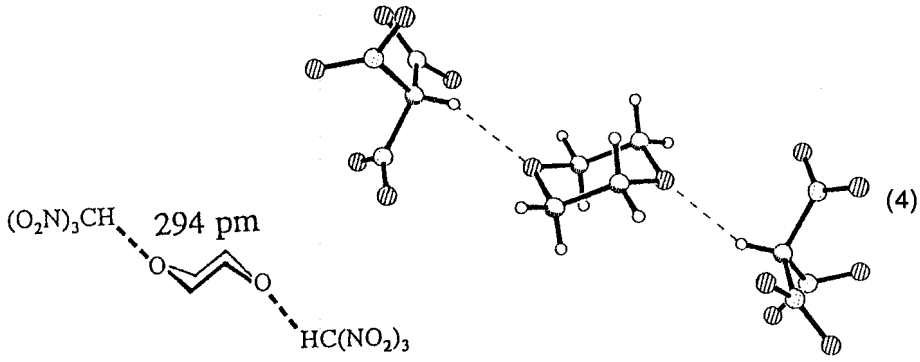


(3)

The aci-diphenylnitromethane dimer (2), therefore, is a remarkable example both for the stabilization of a thermodynamically unfavorable tautomer by H bridge pairs and for molecular self-organization by their cooperative effect.[12]

CH BONDING IN TRINITROMETHANE/DIOXANE AND IN HEXAKIS(TRIMETHYLSILYL)DISILANE

The crystal growth of H bridged aggregates either from solution by using non-protonable counter anions (Figure 3) or from the gasphase by short-pathway sublimation provides access to amusing prototype structures such as the adduct of two trinitromethane molecules to dioxane:[13]



(4)

The single crystal structure determined leaves no doubt concerning the hydrocarbon to oxygen CH···O bond from the rather acidic $(O_2N)_3CH$ and according to the Cambridge Structural Data Base its length of only 294 pm is the shortest one registered so far.[13]

Within this context, van der Waals interactions between methyl groups $CH_3\cdots H_3C$ are brought to attention, which are presumably among the weakest ones structurally provable. They are accessible, for instance, by synthesizing model compounds with spacers of different lengths between the half-shells of bulky tris(trimethylsilyl)silyl and tris(trimethylsilyl)methyl substituents (Figure 4). In hexakis(trimethylsilyl)disilane (Figure 4: B), the space-filling substituents $Si[Si(CH_3)_3]_3$ are connected by a Si-Si bond elongated to 240 pm. Some of the C···C distances between the two molecular halves amount to only 352 pm; that is, they are shortened by 12 % relative to the sum of the van der Waals radii of two methyl groups, which are usually considered to be each about 200 pm.[2] The molecular skeleton $Si_3Si\text{-}SiSi_3$ of D_3 symmetry unexpectedly exhibits two different dihedral angels of 43° and 77° (Figure 4: B and C). Structural comparison with analogous molecules (Figure 4: C) reveals that the dihedral angles ϖ_1 and ϖ_2 between the spacer-linked substituents are different if these are less than 333 pm apart,

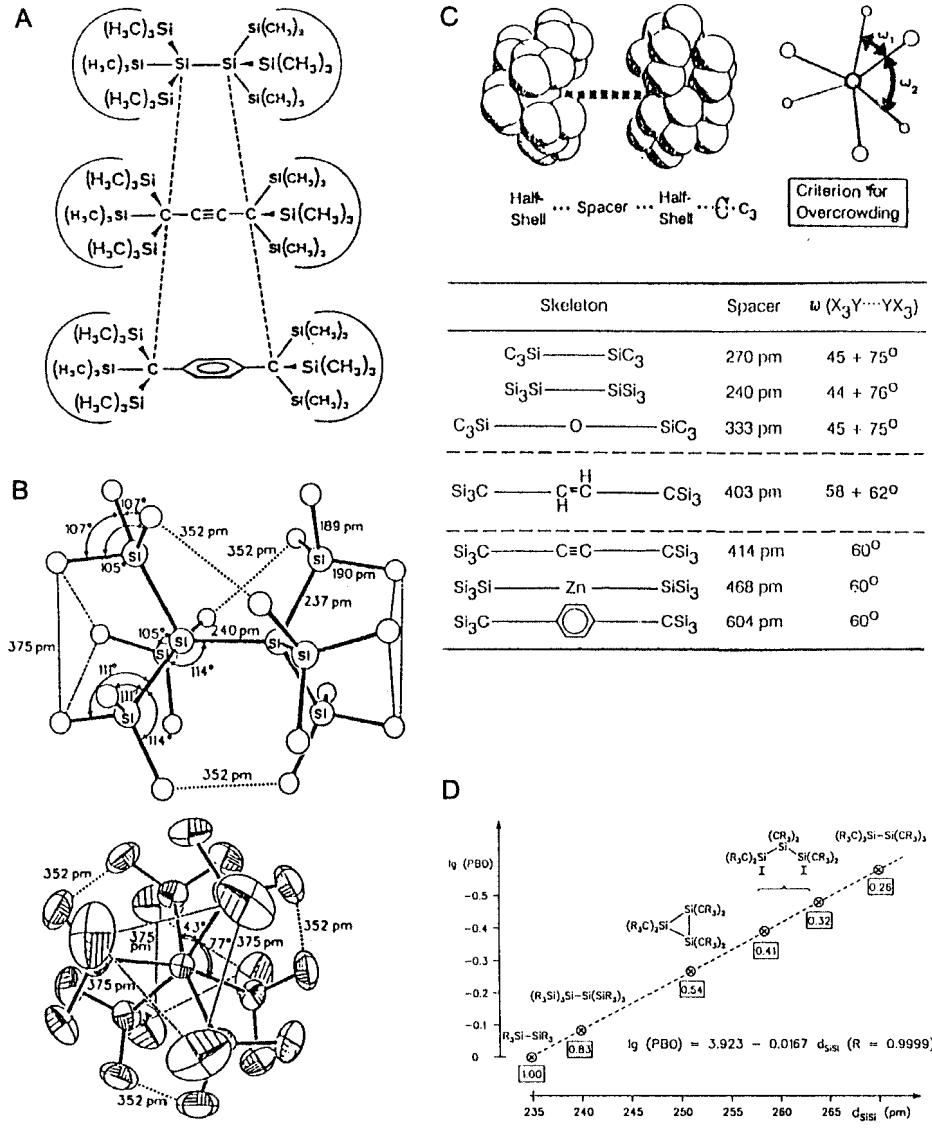


FIGURE 4. (A) Organosilicon model compounds with spacers of different lengths between bulky substituent half-shells. (B) Single crystal structure of hexakis(trimethylsilyl)disilane.[8] (C) Dihedral angle overcrowdedness criterion for half-shell/spacer model compounds of local C_3 symmetry. (D) Pauling bond order/SiSi bond lengths correlation suggesting additional van der Waals attraction in the hydrocarbon skin of overcrowded organosilicon molecules.[5,6,8]

but identical if more than 403 pm apart. Therefore, the twisting $D_{3d} \rightarrow D_3$ of the molecular skeletons from the optimal conformation with $\varpi(X_3Y\text{-}YX_3)$ = 60^o is an appropriate criterion for steric overcrowding, which leads to extremely short C···C van der Waals distances between some of the methyl groups (Figure 1: B) as a result of their additional cogwheel-meshing in the interior of the molecule.

Spatial overcrowding especially due to tris(tert-butyl)silyl substituents (Figure 4: C) with C-C bond lengths which are approximately 40 pm shorter than C-Si ones, stretches the standard Si-Si bond length of 235 pm in hexamethyldisilane to 270 pm and lowers the corresponding Pauling bond order from 1.0 to 0.26. It has been proposed, therefore, that the weakened central Si-Si bonds are strengthened by additional attractive van der Waals interactions in the enveloping hydrocarbon "skin".[9] This assumption would also be compatible with the structure of hexakis(trimethylsilyl)disilane, in which some of the intramolecular C···C distances amount to only 352 pm (Figure 4: B), and also with intermolecular distances found on analysis of the lattice packing. The pronounced van der Waals interactions in and between organosilicon molecules are due presumably to the rather strong polarization $Si^{\delta\oplus}\text{-}C^{\delta\ominus}\text{-}H^{\delta\oplus}$ caused by the low effective nuclear charge of Si centers.[1]

H-BRIDGED POLYMORPHS AND ISOMORPHS

The hierarchy of molecular interactions as determined by their energy sequence and especially the weakness of van der Waals contributions can be demonstrated by the structure comparison of closely related π donor/acceptor complexes (Figure 5).[15] Obviously, a partly herringbone-like packing motif i.e. a van der Waals interaction of σ_{CH}/π-type such as in {perylene/tetracyanobenzene} (Figure 5: top) can be levelled out by superimposing a much stronger H bridge dimer interaction via exchange of tetracyanobenzene for the corresponding tetracyanohydroquinone acceptor[10] (Figure 5: bottom, cf. also Scheme 1).

The structures of polymorphic conformers of the very same molecule as well as the almost identical isomorphic crystals of chemically related and only slightly differing compounds provide multi-faceted information on weak interactions in and between ensembles in crystals. Polymorphism is widely documented in the literature.[5,16]

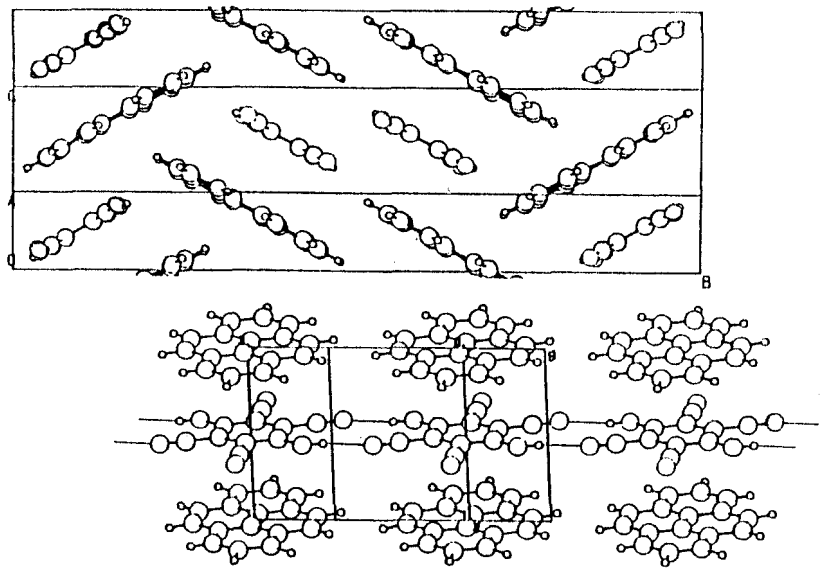


FIGURE 5. Lattice packing of the chemically related π donor/acceptor complexes {perylene/tetracyanobenzene}, exhibiting a herringbone-like motif, and of {pyrene/tetracyanohydroquinone} with a polymer $(OH\cdots NC)_2$ bridged structure (cf. Scheme 1).

For both poly- and isomorphism each one example from the Frankfurt Group will be presented here. Starting with our most spectacular case of tetraisopropyl-p-phenylendiamine $(H_7C_3)_2N\text{-}C_6H_4\text{-}N(C_3H_7)_2$, which crystallizes in both monoclinic and triclinic modifications[16] with the nitrogen lone pairs are either perpendicular to or in the benzene ring plane, we also succeeded in growing different crystals of dipyridylamine both from CCl_4 solution and by vacuum sublimation. In accord with published structure determinations,[17] from CCl_4 solution an orthorhombic modification is obtained (Figure 6: A), whereas vacuum sublimation or crystallization from acetone yields a triclinic one (Figure 6: B). Both contain specific conformations of dimeric dipyridylamine, which exhibit different bond lengths of the N(H)N bridge pairs and differ considerably in the dihedral angles of 46° and 73° between the best planes for the two dimer halves.[17] These amazing and amusing differences between conformational polymorphs of the dipyridyl amine dimer with its N(H)N bridge pairs might well have some biochemical implications.

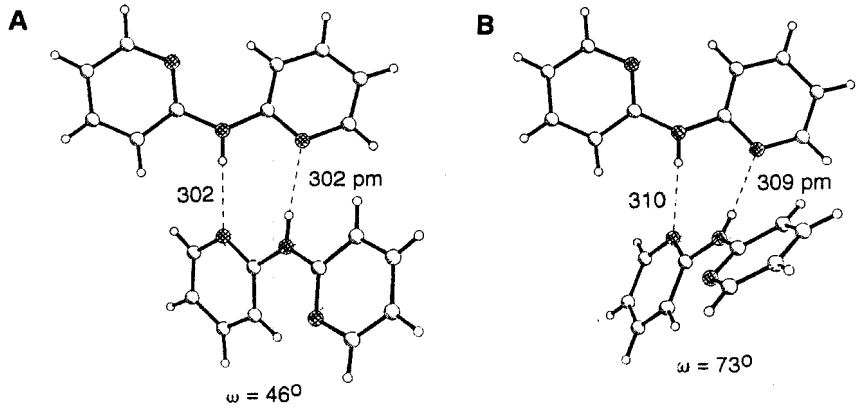


FIGURE 6. Structures of N(H)N pair bridged dipyridyl amine dimers: (A) Orthorhombic modification, crystallized from CCl_4 and (B) triclinic modification, with the crystals grown by sublimation at 310 K and 10^{-2} mbar or from acetone solution[17] (see text).

The isomorphic example presented here (Figure 7) has been discovered serendipitously: Purification of N,N'-ditosyl-p-phenylenediamine - prepared as a precursor to synthesize derivatives RR'N-C_6H_4-NRR' with different alkyl groups at each N center in search of other conformational polymorphs with N lone pairs in or perpendicular to the benzene ring plane - by recrystallization from solvents such as acetone or tetrahydrofurane, unexpectedly, yielded isotypic crystals.[18] Due to the dominating, obviously energetically favorable H bridge dimer $(NH\cdots O(S))_2$ packing motif (Figure 7) even their lattice dimensions are almost identical. Only on recrystallization from solvents with stronger H bridge acceptor centers such as in the pyramidal dimethylsulfoxide, the H bridge dimer is converted to a double $(NH\cdots OS(CH_3)_2)$ bridge adduct, which leads to a completely different packing motif.[18] For the isotypic crystals which can be grown also with inclusion of other solvent molecules such as cyclopentanone, 2-cyclopenten-1-one or 2,3-dihydrofurane, preliminary NMR data allow to conclude that the inclusion of the different solvents at least in some cases produces isomorphs.

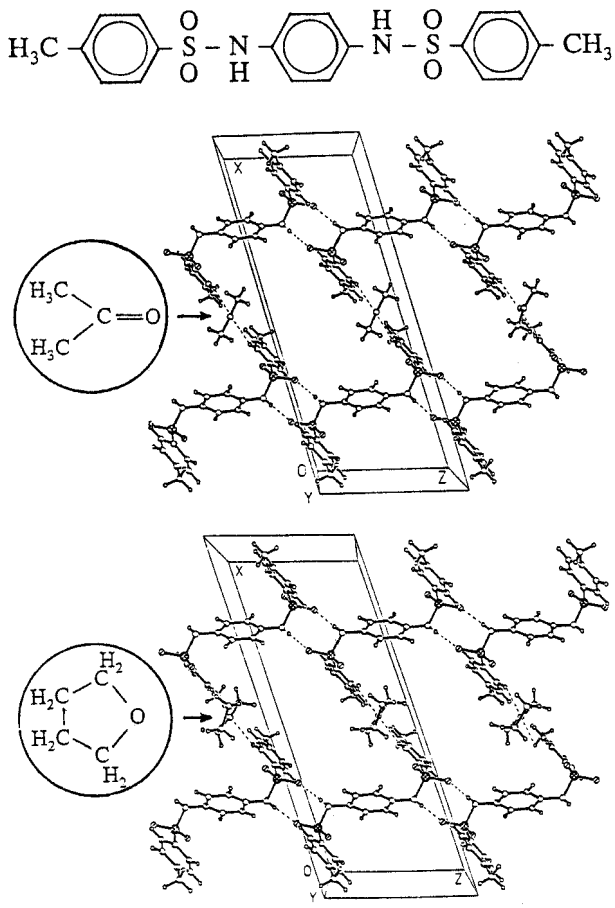


FIGURE 7. Single crystal structures of N,N'-ditosyl-p-phenylene diamine acetone and tetrahydrofurane (space group C2/c, axes a = 2446,2 and 2409,7, b = 1077,9 and 1100,7, c = 938,6 and 943,5 pm).

The six preceding single crystal structures (Figures 5 to 7) illustrate the various types of hydrogen bonding in uncharged molecules - stretching from weak $\sigma_{CH} \rightarrow \pi$ via medium N(HN) pair to massive N(H)OSO interactions, which enforce a specific and favorable lattice packing motif. In addition, the conformational polymorphs as well as the isotypic crystals with different solvent molecules in identical environment provide essential information on crystal-shaping forces.

OUTLOOK: CRYSTALLIZATION - FASCINATION

This interim research report covers two years of fascination by hydrogen bonding, which we studied in addition to structures of charge-perturbed and sterically overcrowded molecules,[2] and another year of increasing packing-mindedness. Starting from preceding investigations on molecular states in the gasphase on short-lived molecules and in solution on paramagnetic species, both experience in relevant measurement methods such as photoelectron or ESR/ENDOR spectroscopy and in quantum chemical rationalization of the resulting measurement data provided useful guidelines for a largely preparative group to learn how to crystallize precalculated charge-distorted, sterically overcrowded or even H bridge containing molecules and to determine their solid state structures.

Based on the experience gathered, we increasingly tackle more complex lattice networks,[6] including those with multiple hydrogen bridge bonding.[19] To present just one of many known N-heterocycle hydrochlorides, crystallized from aqueous solution, dipyridylium hydrochloride dihydrate (Figures 8) is selected,[19] to demonstrate in addition the manifold of H-bonding by this highly attractive model compound (cf. Figure 6). Within the crystal lattice, the two dimensional layer $Cl^{\ominus}(H_2O)_2$ i.e. the interconnected network of chains $(HOH\cdots Cl^{\ominus}\cdots HOH)_{\infty}$ seems to be a well-designed frame for the organic moiety. This raises e.g. the question, whether the one or other biological macromolecule might not be crystallized after adding a "physiological" sodium chloride solution, which would not "denature" the protein component. And it is quite impressing how easily the crystals grow in all their complexity and obviously guided by simple, but still unknown hydrogen bridge formation rules.

In the area of lattice packing analysis we are just beginners, grateful for advices of knowledgeable long-time professionals and heavily relying on the wealth of literature as quoted in our publications.[1-19] And, there are increasingly more questions than answer with regard to "what crystallizes how and why?" or, put positively, there is a lot of stimulation for numerous future experiments.

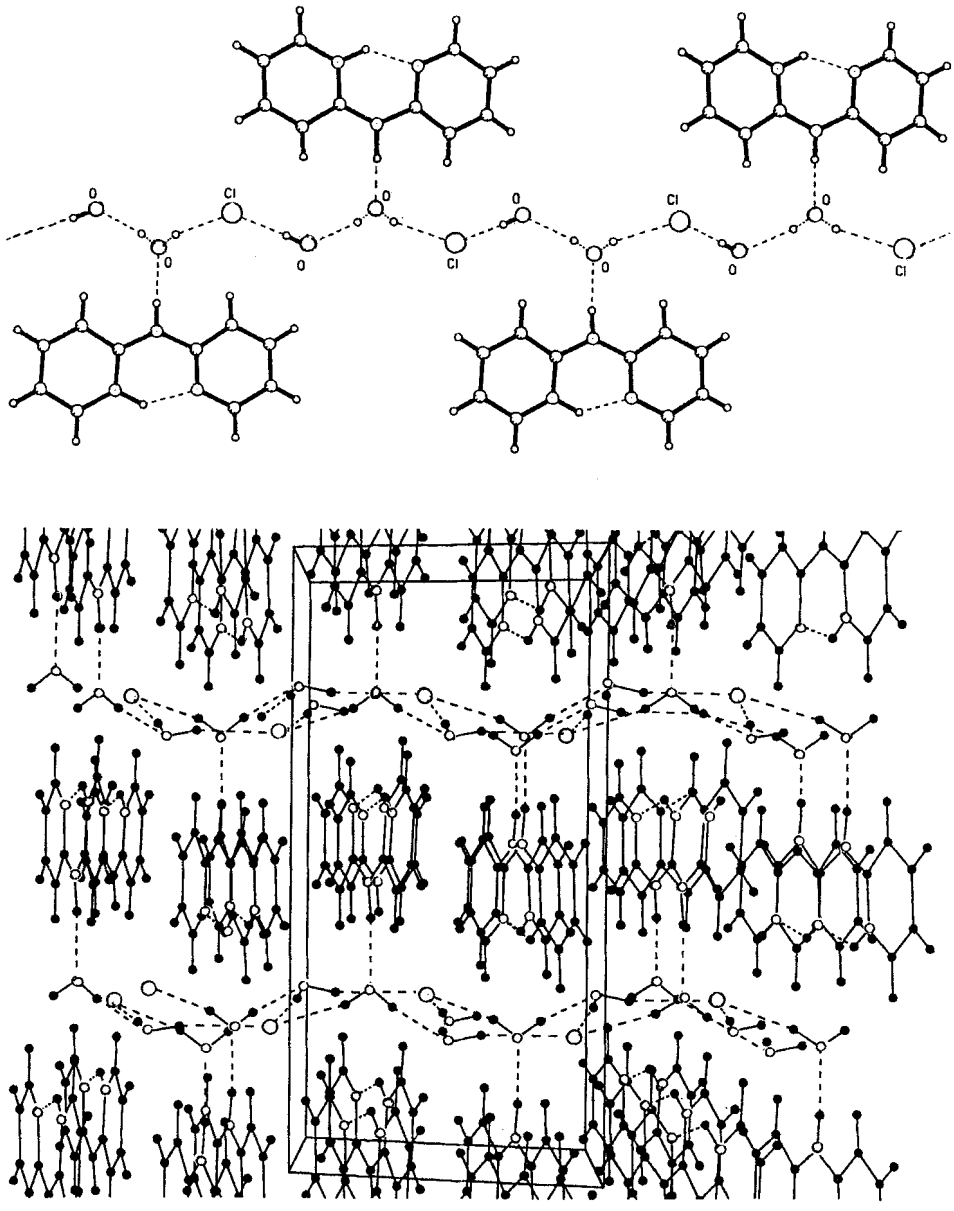


FIGURE 8. Single crystal structure of dipyridylamine hydrochloride dihydrate (cf. Figure 6): (A) One-dimensional view along a chloride dihydrate chain, suspended on dipyridyliumamin heterocycles and (B) the two-dimensional network $Cl^{\ominus}(H_2O)_2$ within in crystal lattice viewed in X-direction.

Acknowledgements: Above all, the achievements of dedicated coworkers are specified as follows: structure determination C. Näther, K. Ruppert and H. Schödel, quantum chemical calculations Z. Havlas and G. Koch, synthesis and crystallization of hydrogen-bridged compounds R. Dienelt. M. Gluth, N. Nagel, H. Schödel, W. Seitz, T. Van and T. Vaupel, charge transfer complexes I. Göbel, A. Rauschenbach, W. Seitz, M. Sievert and K. Ziemer, van der Waals interactions I. Göbel and J. Meuret, polymorphs and isomorphs I. Göbel, A. John, C. Näther, N. Nagel and H. Schödel. Advices for structural solutions from J.W. Bats, W. Bensch and E. Egert (Frankfurt) as well as K. Herdtweck (Munich) are appreciated. Last, but not least we thank A. Gavezzotti and G. Fillipini (Milano) for their cooperation. Our research has been generously supported by the Deutsche Forschungsgemeinschaft, the State of Hesse, the A. Messer Foundation, Fonds der Chemischen Industrie as well as the A.v. Humboldt Foundation.

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