

The supramolecular architecture of 4-aminoacetophenone (1-(4-fluorophenyl)ethylidene)hydrazone hydrate. Double T-contacts and extremely low-density water layers in a mixed azine^{1,2}

Michael Lewis, Charles L. Barnes, and Rainer Glaser

Abstract: The crystal structure of unsymmetrical azine 4-aminoacetophenone (1-(4-fluorophenyl)ethylidene)hydrazone hydrate, $1 \cdot \text{H}_2\text{O}$, was determined. Comparison to the X-ray structures of the symmetrical 4-fluoro- and 4-aminoacetophenone azines, **2** and **3**, respectively, reinforces the view of the azine bridge as a conjugation stopper. The focus of the analysis lies with the supramolecular architecture. The structure demonstrates azines as double T-contact synthons and suggests that novel L-type arene–arene contacts also might play a significant role in the supramolecular architecture. The absence of inter-water hydrogen bonding in an extremely low-density water layer is one of the surprising and unique features of the solid-state structure of the title compound. The water layers connect azine layers through a hydrogen bonded network which is described by graph set analysis.

Key words: arene–arene interaction, hydrogen bonding, graph set analysis, azine, supramolecular synthon, low density water monolayer.

Résumé : On a déterminé la structure cristalline de l'hydrate de la 4-aminacétophénone (1-(4-fluorophényl)éthylidène)hydrazone ($1 \cdot \text{H}_2\text{O}$) (dérivé asymétrique de l'azine de l'acétophénone). Une comparaison de celle-ci avec les structures cristallines des azines symétriques 4-fluoro- et 4-aminacétophénone-azines, respectivement **2** et **3**, confirme le fait que le pont azine arrête la conjugaison. L'analyse se concentre sur l'architecture supramoléculaire. La structure démontre que les azines agissent comme synthons à doubles contacts-T et elle suggère la possibilité que de nouveaux contacts arène-arène de type-L puissent jouer un rôle significatif dans l'architecture supramoléculaire. L'absence de liaison hydrogène entre molécules d'eau dans une couche aqueuse de densité extrêmement faible est l'une des caractéristiques surprenantes et uniques de la structure à l'état solide du composé mentionné dans le titre. Les couches d'eau connectent les couches d'azines par le biais d'un réseau de liaisons hydrogènes que l'on décrit à l'aide d'une analyse d'un ensemble de graphes.

Mots clés : interaction arène–arène, liaison hydrogène, analyse d'un ensemble de graphes, azine, synthon supramoléculaire, monocouche d'eau de faible densité.

Introduction

We have been interested in the linear and nonlinear optical properties of *N*-perturbed donor–acceptor asymmetric conjugated systems of the azine type. As a first step toward the elucidation of the underlying electronic structures and properties, we have systematically studied the crystal structures and the packing of symmetric (**1**, **2**) and unsymmetric

(**3**–**5**) acetophenone azines. These acetophenone azines have the general formula $\text{X-Ph-C(Me)=N-N=C(Me)-Ph-Y}$, and they are called symmetric if $\text{X} = \text{Y}$ and unsymmetric in the case $\text{X} \neq \text{Y}$ (see Appendix). Our studies have resulted in the first realization of two prototypes of molecular organic materials with near-perfect dipole parallel-alignment in the pure crystal of the mixed azines 4-bromo- and 4-chloro-acetophenone (1-(4-methoxyphenyl)ethylidene)hydrazone (**3**, **4**)^{4,5}.

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⁴The piezoelectric material 4-bromo-4'-methoxyacetophenone azine has been featured as the “Molecule of the Month, December 1997” on the World Wide Web, and its crystal structure can be viewed at URL <http://www.bris.ac.uk/Depts/Chemistry/MOTM/motm.htm>.

⁵X-ray structures of the organic piezoelectric 4-chloro-4'-methoxyacetophenone azine. R. Glaser, M. Lewis, and C.L. Barnes. In preparation.

Scheme 1.

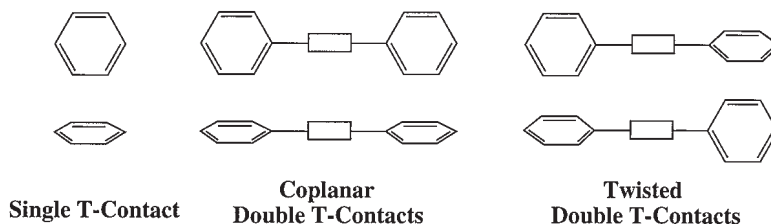
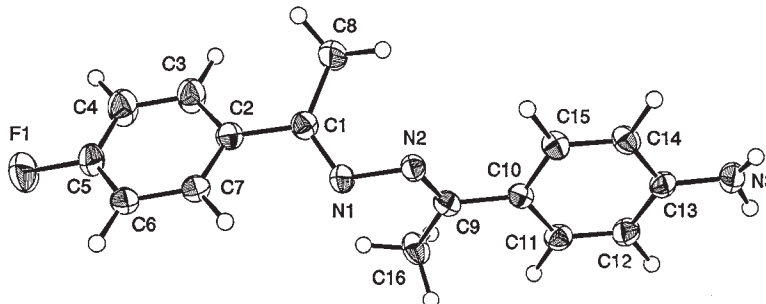


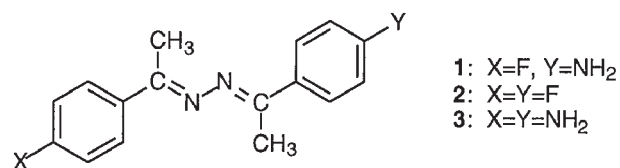
Fig. 1. ORTEP II drawing of mixed azine **1**. Major bond lengths in angstroms are F1—C5 = 1.3605(25), C2—C1 = 1.480(3), C1=N1 = 1.286(3), N1—N2 = 1.4140(23), C9—N2 = 1.293(3), C9—C10 = 1.480(3), and C13—N3 = 1.374(3).



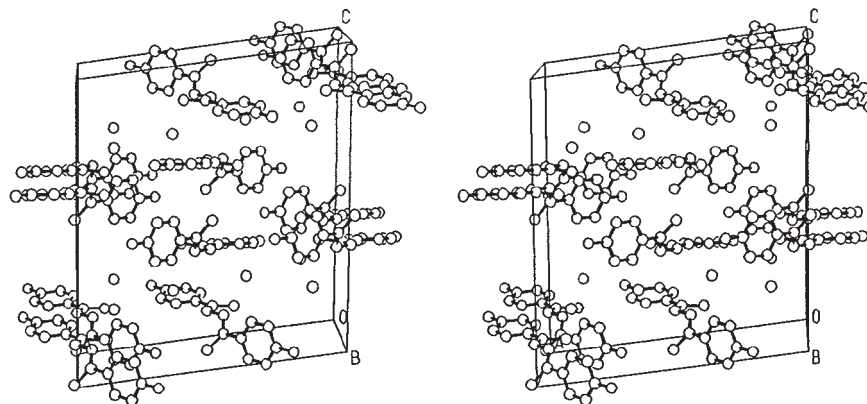
Non-centrosymmetry is a necessary requirement for all types of polar effects of crystals (6) (nonlinear optical (NLO) activity, piezo- and pyroelectric effects, and many others) but it is not a sufficient requirement. Many organic compounds crystallize in chiral space groups (7) without realizing any significant macroscopic polar effects (8, 9). The proper alignment of the polar building blocks is the pertinent issue, and the creation of large crystal polarizations remains a challenge beyond the simple quest for non-centrosymmetry. The *de novo* design of crystals is an undertaking of extraordinary difficulty since the lattice architecture results from the optimization of a large number of weak intermolecular interactions. These interactions are far too complex to trace and, thus, also far too complex to create by pure design. Olson (10) recently pointed out that the simplifying methods of scientific analysis can contribute to meeting this challenge when such analyses are pursued within the systems approach of engineering. Central to the systems approach is the sequential, deep and rigorous scientific analysis of a small number of prototypes. It is the goal of the prototype analysis to recognize significant intermolecular interactions. Molecular fragments capable of binding with certain other atoms or functional groups with high selectivity and high affinity are referred to as synthons (11, 12). The crystal structures of the prototypes of the ferroelectric azines show pairs of perfectly parallel aligned unsymmetrical azine molecules with two T-contact arene–arene interactions. The azine spacer is special in that its conformational flexibility (13) allows for near-orthogonality between the two benzenes in the same azine. The Ph-CR=N-N=CR-Ph system thus constitutes a “double T-contact synthon” and we believe this motif to be key to understanding the suprastructures of the prototypes. Double T-contacts occur when the arene rings of two compounds containing two arene groups each stack in such a way that two edge-to-face arene–arene contacts are realized. Scheme 1 illustrates the two possibilities for double T-contacts.

Coplanar double T-contacts result when the arene rings of each bisarene compound are (more or less) in the same plane. Thus, if the spacer between the two aromatic rings is unsaturated, there exists the possibility of conjugation. Twisted double T-contacts require the arene rings of each bisarenes to be (more or less) orthogonal. This situation can only occur through a twisting of the spacer between the arene rings, and therefore one would not expect any conjugation between the arene rings.

As part of our studies of unsymmetrical acetophenone azines we have now prepared the mixed azine 4-aminoacetophenone (1-(4-fluorophenyl)ethylidene)hydrazone (**1**, Fig. 1), and here we report the crystal structure of its hydrate,



1·H₂O. We have previously reported the solid-state structures of the respective symmetrical azines **2** (X = Y = F) and **3** (X = Y = NH₂) (2), and these data present the best possible reference to discuss the structural effects of asymmetrization. The structure of **1** demonstrates the importance of the double T-contact synthon. The superstructure of the title compound also is unique in two further respects. First, the supramolecular architecture of **1** features not only T-type arene–arene interactions but also exhibits highly perturbed T-contacts that can be described as L-type van-der-Waals arene–arene interactions. The other interesting feature relates to the occurrence of water layers which are exceptional in that there is no hydrogen bonding between the intra-layer water molecules.

Fig. 2. Packing of azine hydrate **1**·H₂O.

Results and discussion

Structural effects of asymmetrization and the question of π -conjugation

The ORTEP II diagram of **1** is shown in Fig. 1, and a view of the packing of **1**·H₂O is shown in Fig. 2. The crystallographic data for **1**·H₂O is presented in Tables 1–3. At first glance the title compound **1** appears to be a classical example of a donor–acceptor molecule which allows for donation of electron density from the amino-substituted phenyl ring into the fluoro-substituted phenyl ring. However, Fig. 1 reveals that mixed azine **1** is not planar, but rather the $>C=N-N=C<$ bridge assumes a *gauche* conformation ($\tau = 56.4^\circ$) and the phenyl rings both are twisted more or less out of the conformation that would be best for conjugation. The amino-substituted phenyl ring is twisted only slightly by $\phi_1 = 8.4^\circ$ out of the plane defined by the *ipso*-carbon and the atoms of the C9=N2 imine bond and still allows for through conjugation from the amino group to the imine functionality. Conversely, the fluoro-substituted phenyl ring is twisted by $\phi_2 = 31.2^\circ$ out of the plane defined by the *ipso*-carbon and the C1=N1 imine bond, eliminating all possibilities for through-conjugation. Since the C2—C1, N1—N2, and C9—C10 bonds in **1** are almost parallel, the sum of τ , ϕ_1 , and ϕ_2 provides an excellent approximation for the angle ω between the best planes through the benzene rings. Recognizing that τ and ϕ_i all serve to increase ω , this approximation gives $\omega \approx 96.0^\circ$ and leaves the benzenes nearly orthogonal. Rather than considering the azine spacer a conjugating bridge in an extended donor–acceptor system, the azine bridge in **1** acts more like a “conjugation stopper,” a term we introduced earlier to describe the electronics of asymmetric acetophenone azines. In this model the azine bridge is viewed as two oppositely oriented imine acceptors. The azine **1** should thus present itself as a system with a dipolar donor–acceptor half with an NH₂-donor and a C9=N2 imine bond acceptor, and an essentially quadrupolar half, where both the F and the C1=N1 imine bond are acceptors. Comparison with the symmetrically substituted azines **2** and **3** reinforces the view for the azine bridge as a conjugation stopper. The NH₂-half of **1** is perturbed very little as compared to the NH₂-halves for the symmetrical azine

3. The average C_{*ipso*}—NH₂, C9—C10, and N2—C9 bond lengths in **3** are 1.38, 1.48, and 1.29 Å, respectively. These bond lengths are identical to the corresponding C9—C10 and N2—C9 bond lengths in **1**. The C_{*ipso*}—NH₂ is marginally less for **1** at 1.37 Å and a small discrepancy is to be expected since **1** crystallizes into a different H-bonded network than **3**. The same trend is present when comparing the F-half of **1** with azine **2**. The average C_{*ipso*}—F bond length is 1.36 Å for **2**, while the bond lengths that correspond to C2—C1, and C1—N1 are 1.48 and 1.28 Å, respectively. These bond lengths are identical to the corresponding bond lengths in **1**, except for C1—N1 which is 1.29 Å long.⁶ Once again, a small variation is to be expected since **1** and **3** are in different crystal environments. Thus, the six bond lengths that would be affected most by through conjugation in fact remain almost unperturbed.

Double T-contacts in the van der Waals bonded azine layers

The crystal lattice (Fig. 2) of **1**·H₂O contains alternating layers of azines and water molecules stacked in the direction of the *c*-axis. Each azine layer is rotated by 90° from the azine layer below or above it and consists of inversion-symmetric pairs of dipole antiparallel-aligned azines with N–N *gauche* conformations (Fig. 3a). In the *P/M* nomenclature for the chirality of conformational isomers (14), the top structure of the azine pair depicted in Fig. 3a has *M* helicity, while the bottom structure has *P* stereochemistry. The azine pairs in Fig. 2 are characterized by two identical intermolecular arene–arene T-contacts (15, 16) that can best be described as twisted double T-contacts (Scheme 1). The near perpendicular phenyl arrangement ($\omega \approx 96.0^\circ$) in **1** might be adopted to take full advantage of these intermolecular double T-contacts. A priori there is a choice as to which of the substituted benzenes serves as the vertex or the head of the T-contact. In the crystal structure of **1**, we find that the F-substituted benzenes always serve as the vertices. It is possible that polymorphs might exist with the opposite arrangement. The contact distance between the two phenyl rings ranges from 3.6 to over 4.1 Å (Fig. 3b). Alternatively, the layering of **1** along the direction of the *c*-axis can be described as involving two azine monolayers between water

⁶The estimated standard deviations (esd's) for the bond distances discussed in this section are on the order of thousandths of angstroms. Since we only cite the bond distances to hundredths of angstroms, these very small esd's strengthen our arguments.

Table 1. Crystallographic data.

Crystal data	
Source of material	CHCl ₃
Crystal shape, colour, and size	Thin wafers, yellow, 0.15 × 0.20 × 0.45 mm
Empirical formula	C ₁₆ H ₁₆ N ₃ F·H ₂ O
Formula weight	287.33
Crystal system	Monoclinic
Space group	C2/c
Unit-cell dimensions	$a = 17.2988(12)$, $b = 8.9205(6)$, $c = 19.3557(15)$ $\alpha = 90.0$, $\beta = 97.5870(10)$, $\gamma = 90.0$
Number and θ range of reflections	4045 reflections, $10^\circ \leq \theta \leq 50^\circ$
Volume of unit cell	2960.7(4) Å ³
Z	8
D_{expt}	1.289 g/cm ³
D_{meas}	Density not measured
Radiation and wavelength	$\lambda(\text{Mo-K}\alpha) = 0.70930$ Å
Linear absorption coefficient	0.09 mm ⁻¹
Temperature of measurement	293 K
Data collection	
Diffractometer	Siemens Smart CCD system
Method used to measure diffraction data	Omega scan mode
Absorption correction	Data were corrected for decay and absorption using the program SADABS based on the method of Blessing (30)
Number of reflections measured	8416
Number of independent reflections	3212
Number of observed reflections	2413
Criteria for recognizing observed reflections	$I > 2.0\sigma(I)$
Maximum value of q	$2q_{\text{max}} = 54.0^\circ$
Range of h , k , and l	$-22 \leq h \leq 21$, $0 \leq k \leq 11$, $0 \leq l \leq 24$
Refinement	
Use of F , F^2 , or I	Refinement on F
$R = \Sigma(F_o - F_c)/\Sigma F_o $	0.053
$wR = \{\Sigma[w Ym - Yc ^2]/\Sigma(wY^2m)\}^{1/2}$	0.079
Method of refining and location H atoms	Water and amino hydrogen atoms were located from a difference map, and refined with fixed isotropic thermal parameters. Ring and methyl hydrogen atoms were placed at calculated positions.
Number of parameters	202
Number of reflections used in refinement	2413
GOF $\{ = [\Sigma w(Ym - Yc)^2/(m - n)]^{1/2} \}$	1.34
Definition of w	$w = 1/[\sigma^2(F) + 0.002(F^2)]$
Maximum $\Delta\sigma$	0.004
Maximum and minimum $\Delta\rho$ in final difference electron density map	max = 0.260 and min = -0.220 e Å ⁻³
Source of scattering factors	<i>International Tables for X-ray Crystallography</i> (1974)
All computer programs used	NRCVAX (E.J. Gabe et al., 1989)

layers and from this vantage point the T-contacts are responsible for the cohesion between the azine monolayers. Each of these azine monolayers is completely dipole aligned but in opposite directions.

The inter-pair packing between azines in each respective layer also occurs via arene–arene interactions. These contacts are highly distorted T-contacts, and they might also be described as L-type arene–arene interactions (Fig. 3c). Arene–arene interactions have been studied extensively by ab initio (15, 17), Monte Carlo (18), and molecular mechanics (19) theoretical methods, using Raman (20), NMR (21),

and mass selective hole-burning (22) spectroscopic techniques and also by solid-state X-ray crystallography (23). These studies produced a vast body of evidence for the significance of face-to-face and T-contacts, however there is no evidence for T-contacts perturbations that lead to L-contacts. There are many examples of perturbed T-contacts of the herringbone motif (15–17a) which are the result of non-orthogonal (and slipped) vertices. The L-contact exhibited in **1** is the result of a strong perturbation of the T-contact with the rings remaining perpendicular (Fig. 3d). Since the C_J–C_I bond is coplanar with the benzene ring shown on the

Table 2. Positional and equivalent isotropic thermal parameters, with esd's in parentheses.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{iso}
F1	0.29633(9)	0.64047(18)	0.46105(8)	4.57(7)
O1	0.13773(9)	0.13243(17)	0.24282(9)	2.74(6)
N1	0.05454(10)	0.13509(19)	0.36419(9)	2.19(6)
N2	-0.00547(9)	0.02665(18)	0.35361(8)	2.10(7)
N3	-0.21184(12)	-0.56854(22)	0.30191(10)	2.62(8)
C1	0.05192(12)	0.22602(23)	0.41535(10)	2.25(7)
C2	0.11382(12)	0.34130(23)	0.42623(10)	2.27(8)
C3	0.13973(15)	0.3931 (3)	0.49370(12)	3.29(9)
C4	0.20119(15)	0.4946 (3)	0.50574(13)	3.71(10)
C5	0.23549(13)	0.54301(25)	0.44970(13)	3.01(9)
C6	0.21016(12)	0.49996(24)	0.38224(12)	2.55(8)
C7	0.14897(12)	0.39792(22)	0.37107(11)	2.30(8)
C8	-0.00801(15)	0.2166 (3)	0.46479(13)	3.62(10)
C9	0.01790(11)	-0.11112(22)	0.35399(10)	2.04(8)
C10	-0.04224(11)	-0.22936(22)	0.34095(9)	1.92(7)
C11	-0.02158(12)	-0.37929(24)	0.33228(11)	2.41(8)
C12	-0.07668(13)	-0.49152(23)	0.31903(11)	2.54(8)
C13	-0.15621(12)	-0.45824(22)	0.31350(10)	2.15(8)
C14	-0.17775(12)	-0.30911(23)	0.32385(11)	2.32(8)
C15	-0.12209(12)	-0.19767(22)	0.33741(11)	2.28(8)
C16	0.10195(12)	-0.1576 (3)	0.36842(12)	2.83(9)

right (containing C_k), and since the atoms C_i , C_j , and C_k lie in a plane that is almost perpendicular to the molecular planes of both phenyl rings, the angle $(C_i, C_j, C_k) = 89.8^\circ$ shows that the benzene planes are essentially perpendicular. It is for these reasons that we refer to this arrangement as an L-contact. As was the case for the intra-pair packing, the F-substituted phenyl rings serve as the vertices in the inter-pair arene–arene interactions. The distance between the L-packed arene rings ranges from 3.556 to 4.142 Å (Fig. 3d) for the edge-to-edge contacts illustrated in Fig. 3c. Note that the realization of the L-contacts requires a translation of neighboring azines within each monolayer along their long molecular axis such that an X-substituted benzene interacts with a Y-substituted benzene. In the absence of such a translation, the packing might benefit from face-to-face stacking of the F-substituted arenes but the amino-substituted benzenes would not be in any favorable position. It has been noted that benzene aggregates do not assume one rigid structure (24) but instead there are a variety of geometries that can be adopted (15). Thus, the formation of the L-contact should not be an entirely surprising result, as the intermolecular forces that govern arene–arene interactions are weak and could be overcome with relative ease due to a variety of competing non-covalent interactions.

Graph set analysis of the hydrogen bonding and low-density water layers

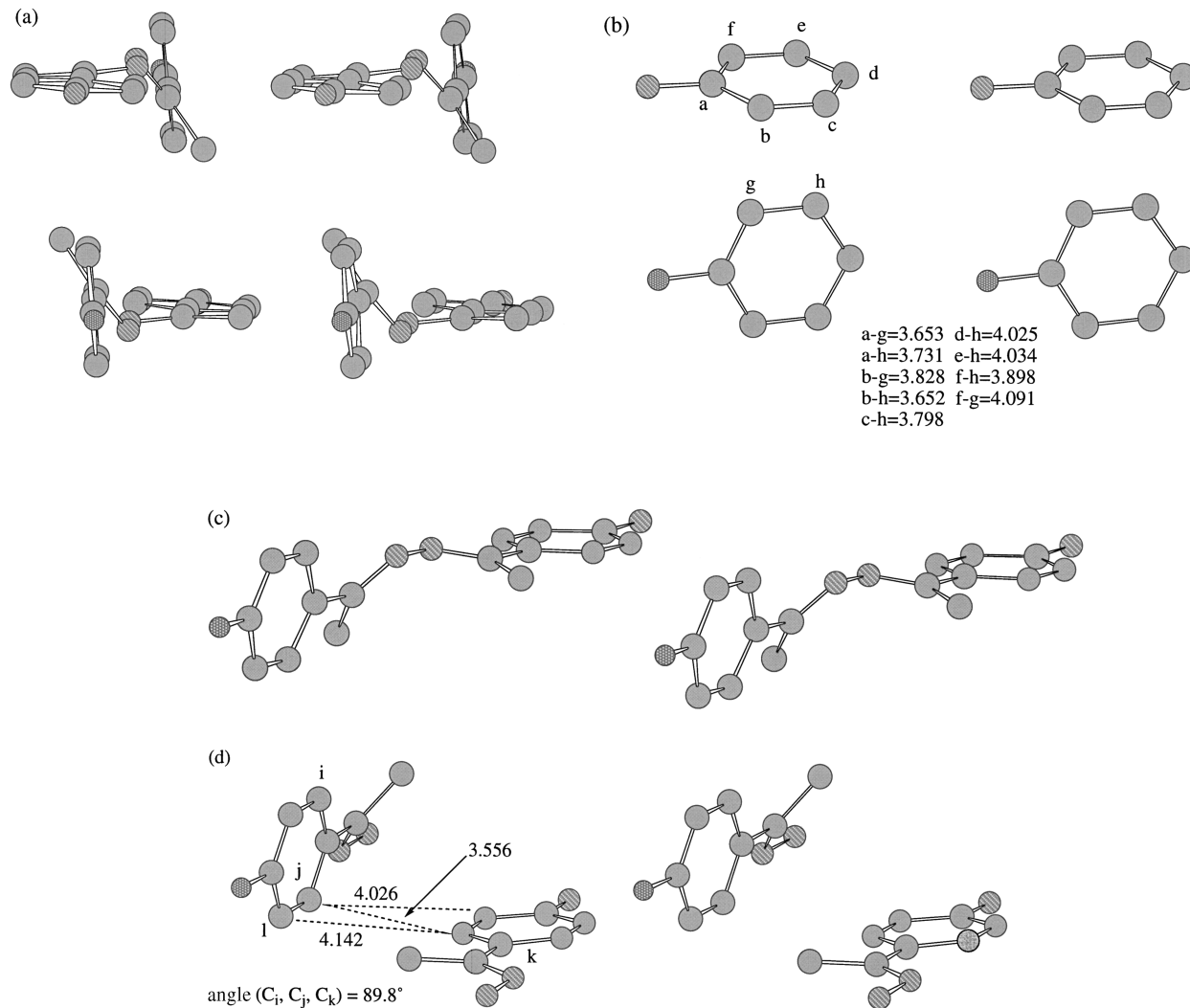
As illustrated in Fig. 2, the azine layers in **1** are held together by layers of water molecules. The positions of the water H-atoms were determined, and the water molecules do not engage in any water–water hydrogen bonding. The water molecules all are aligned such that their molecular planes are nearly parallel with the *ac*-plane, and all of the water dipole moments are nearly colinear with the crystallographic *a*-axis. Each water participates in four hydrogen bonds with

Table 3. Selected bond lengths (Å), angles (°), and selected torsion angles (°).

F1—C5	1.3605(25)	N3—C13	1.374(3)
N1—N2	1.4140(23)	C1—C2	1.480(3)
N1—C1	1.286(3)	C9—C10	1.480(3)
N2—C9	1.293(3)		
N2-N1-C1	116.32(17)	F1-C5-C6	118.30(21)
N1-N2-C9	115.23(16)	N2-C9-C10	117.65(17)
N1-C1-C2	116.72(18)	C9-C10-C11	121.10(17)
C1-C2-C3	119.87(19)	C9-C10-C15	122.03(18)
C1-C2-C7	121.64(18)	N3-C13-C12	121.44(19)
F1-C5-C4	118.65(20)	N3-C13-C14	120.58(19)
C1-N1-N2-C9	-123.6(4)	N1-N2-C9-C10	-178.1(4)
N1-C1-C2-C7	29.57(21)	N1-C1-C2-C3	-148.8(4)
N2-C9-C10-C15	-8.35(18)	N2-C9-C10-C11	172.3(4)
N2-N1-C1-C2	-179.1(4)		

four separate azines (Fig. 4). The hydrogen bonding network is best revealed via the graph set theoretical description proposed by Bernstein and Davis (25). Using their notation, the H_a - and H_b -bonds have unitary graph set notation $N_1 = DD$, indicating that each hydrogen bond H_a and H_b is finite. These two hydrogen bonds are formed between a water acting as a H-donor and an azine N-atom. The system of Bernstein and Davis also allows for more complex graph sets. A binary graph set describes a pattern in which only two types of hydrogen bonds are present, whereas systems with more than two hydrogen bonds can be described by complex basis sets. The hydrogen bonded pattern produced by H_a and H_b has a binary graph set of $N_2(a,b) = C_2^2(5)$ and a complex graph set of $N_2(a,b) = R_4^4(10)$ (Fig. 4a). We exemplify the meaning of the binary graph set for $N_2(a,b) = C_2^2(5)$. The term $N_2(a,b)$ denotes a graph set with two types of hydrogen bonds, H_a and H_b . $C_2^2(5)$ indicates a chain (C) which contains two hydrogen bond acceptors (superscript) and two hydrogen bond donors (subscript) and covers five atoms linked by either covalent or hydrogen bonds. Similarly, the complex graph set R denotes a ring pattern consisting of four donor and four acceptor sites in a 10-membered ring. The other types of hydrogen bonds H_c and H_d both involve water as the hydrogen bond acceptor and the amino groups are the hydrogen bond donors (Fig. 4b). The amino groups are slightly pyramidalized (sum of angles at $N = 354.2^\circ$) and the direction of pyramidalization is such as to suggest optimization of the hydrogen-bonding interactions. The bonds H_c and H_d can be described by a unitary graph set, $N_1 = DD$, and a binary graph, $N_2(c,d) = C_2^1(4)$. In this case, however, there is no complex graph set that relates H_c and H_d . Finally, there also exists two complex graph sets that describe the patterns created by H_a , H_c , and H_d and by all four hydrogen bonds. The pattern produced by H_a , H_c , and H_d has the complex graph set $N_3(a,c,d) = R_4^3(14)$ and is illustrated in Fig. 4c by the thick broken lines. The pattern relating all four hydrogen bonds can loosely be described by the complex graph set $N_4(a,b,c,d) = R_8^7(24)$. This description does not strictly adhere to the notation of Bernstein and Davis because the pattern created by all four hydrogen bonds is not a ring. Instead, a spiro motif exists where the

Fig. 3. All distances are in angstroms. (a) Stereodrawing of the intra-pair azines with almost perfect double-T-contacts. The stereochemistry is such that the top and bottom azines have *M*- and *P*-helicity, respectively. (b) Stereodrawing of the phenyl–phenyl contact for one of the T-contacts shown in (a). (c) Inter-pair contact between azines showing an L-contact motif. (d) Stereodrawing emphasizing the L-contact shown in (c).



ring created by the graph set $N_3(a,c,d) = R_4^3(14)$ shares a common oxygen with the ring created by the graph set $N_2(a,b) = R_4^4(10)$ (the latter ring is shown in Fig. 4c by the thin broken lines). This spiral pattern of hydrogen bonds reveals the infinite two-dimensional layer which acts as the glue that holds the layers of azine pairs together. It appears that the water layer in **1** represents the least dense arrangement of water molecules in the solid state observed to date. The O—O distances of 4.81 and 5.90 Å correspond to a density of approximately one half that of ice I and II (average O—O distance of 2.79 Å (26)). This extreme low density is attributed to the absence of inter-water H-bonding. The unique arrangement of water molecules in **1**·H₂O represents a first for infinite water layers, and it is attributed to the presence of a strong H-bond acceptor in the form of the amino-N atom. The literature on hydrates shows structures of two general classes. The first family of hydrates realizes crystal lattices in which the water molecules hydrogen bond with each other (27) and the other class contains water molecules that are interspersed throughout the crystal lattice (28).

Neither of these classes of hydrates show any water aggregates with cavities. It appears that the infinitely ordered water sheet of the kind demonstrated by **1**·H₂O is entirely unprecedented.

Experimental

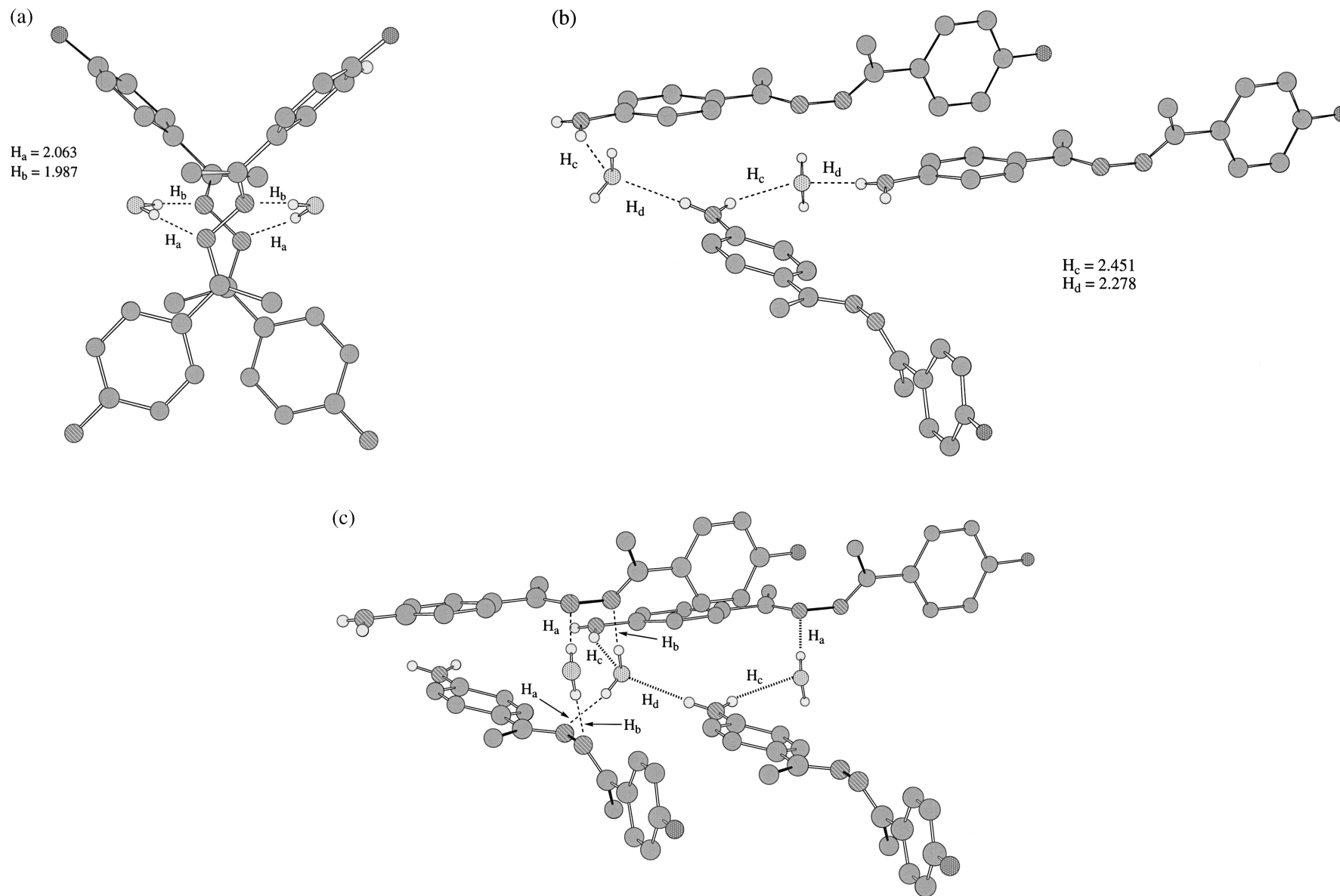
Synthesis and recrystallization

Mixed azine **1** was prepared via hydrazono-de-oxo-bisubstitution (29). Hydrazine hydrate was added to *p*-aminoacetophenone in ethanol to yield the corresponding hydrazone. Reaction of the hydrazone with *p*-fluoroacetophenone in ethanol in the presence a few drops of glacial acetic acid afforded the azine which was purified by column chromatography (hexane–ethylacetate gradient elution). Crystals of the hydrate **1**·H₂O were grown by slow diffusion of hexane into a solution of **1** in chloroform.

Crystal structure determination

A single crystal X-ray analysis was performed on the hydrate (C₁₆H₁₆N₃F·H₂O, *M_r* = 287.33). The compound **1**·H₂O

Fig. 4. All distances are in angstroms. (a) The water H atoms act as the hydrogen bond donors, while the azine-N atoms are the acceptors. By only considering the two unique hydrogen bonds H_a and H_b , the binary basis set $N_2(a,b) = C_2^2(5)$ is realized. The complex basis set $N_2(a,b) = R_4^4(10)$ is a result of two binary sets forming a circle. (b) The amino-H atoms act as hydrogen bond donors, and the water-O atoms are the acceptors. The two unique H-bonds H_c and H_d can be described by the binary basis set $N_2(c,d) = C_2^2(4)$. There is no complex basis set relating H_c and H_d . (c) The complex basis set $N_4(a,c,d) = R_4^4(14)$ is obtained by considering the hydrogen bonded system described by the thick broken lines. All four hydrogen bonds are related by the spiral motif created by the graph sets $N_2(a,b) = R_4^4(10)$ and $N_4(a,c,d) = R_4^4(14)$.



crystallizes in a monoclinic lattice (space group $C2/c$, $a = 17.2988(12)$, $b = 8.9205(6)$, $c = 19.3557(15)$ Å, $\beta = 97.5870(10)^\circ$). Final R factor = 0.053 and wR factor = 0.079 for 2413 reflections with refinement on F and 202 parameters and the GOF value was 1.34. Tables of crystal data, structure solution and refinement, atomic coordinates, bond lengths, and anisotropic thermal parameters for $1 \cdot H_2O$ (12 pages print) have been deposited as supplementary material.⁷

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Appendix

Nomenclature of azines: azines are 2,3-diazabutadienes, they are characterized by the functional group $>C=N-N=C<$, and they formally are the products of condensation between hydrazine and two carbonyl compounds. Symmetrical or unsymmetrical (or mixed) azines are formed, respectively, if the two carbonyl compounds are the same or different. Azines have the general formula $RR'C=N-N=CRR'$, and they are named substitutively as an assembly of identical units using the prefix "azino-." According to functional class nomenclature, they may be named by adding the class name "azine" as a separate word after the name of the corresponding aldehyde or ketone. Hence, $Me_2C=N-N=CMe_2$ is called azinoacetone or, more frequently, acetone azine (see http://www.acdlabs.com/iupac/nomenclature/93/r93_469.htm). In the IUPAC nomenclature, the unsymmetrical azines $RR'C=N-N=CR'R''$ are named as alkylidenehydrazones. Hence, $Me_2C=N-N=CH_2$ can be called formaldehyde (isopropylidene) hydrazone or acetone (methylidene) hydrazone.

⁷Supplementary material and the results of the crystal structure analysis may be purchased from: The Depository of Unpublished Data, Document Delivery, CISTI, National Research Council of Canada, Ottawa, Canada, K1A 0S2. With the exception of isotropic and anisotropic thermal parameters, these and the crystal structure (in CIF format) have also been deposited with the Cambridge Crystallographic Data Centre and can be obtained on request from: The Director, Cambridge Crystallographic Data Centre, University Chemical Laboratory, 12 Union Road, Cambridge, CB2 1EZ, U.K.