The crystal structure of 4-iodoacetophenone azine

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4-Iodoacetophenone azine crystallizes in the space group Pbcn with cell parameters $a = 34.5187(19)$, $b = 7.2638(4)$, and $c = 6.3736(3)$ Å. The azine shows a *gauche* conformation with regard to the N—N bond and the phenyl rings are twisted in a way that leads to the largest possible twist between the benzene rings of each azine. This azine conformation allows for intermolecular arene–arene T-contacts between pairs of benzene rings and these double-T contacts involve only molecules within the same layer. All azines are perfectly colinear within each layer and this results in a quadrilateral kite-shaped arrangement of iodine atoms at the interface of each layer. The iodine-iodine distances within each layer are 4.5 and 5.1 Å, and the three unique angles of the kite-shaped quadrilaterals are 97.1, 76.9, and 88.8°. The iodine atoms in adjacent layers pack such that atoms of one layer fill the square interstices of the next layer. The distances between iodine atoms in adjacent layers are 4.5 and 4.1 Å. The C—I bonds are not orthogonal to the I-planes and the direction of the molecules in adjacent layers causes a deviation of about 40° from colinearity.

Introduction

We have been investigating the stereochemistry,[1–4] electronics,[1,4,5] and crystal packing[1,4,6,7] of symmetric and unsymmetric azines. An azine is the condensation product between two carbonyl molecules and hydrazine. The azines that we have studied have the general structure shown in Scheme 1, and they
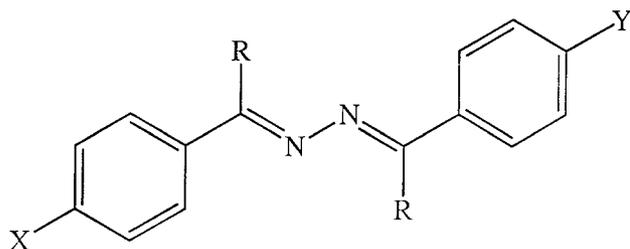
Scheme 1

are called symmetric if X=Y and unsymmetric, or mixed, if $X = Y$. The symmetric[3] and unsymmetric[4,6,7] azines that we have investigated all have an N—N *gauche* conformation about the azine bridge. The N—N *gauche* conformation, in conjunction with a phenyl ring twist, causes the two phenyl rings to be near orthogonal, and this allows for the arene-arene double T-contact throughout the lattices of the previously studied azines. A double T-contact occurs when the two phenyl rings of one spacer-connected biphenyl system interact with the two phenyl rings of another such molecule to form two intermolecular arene-arene T-contacts. Scheme 2 illustrates four types of double arene-arene contacts; **I, II** and **III** are all double T-contacts and **IV** is a double face-to-face contact. Type **I** has a planar spacer and the two phenyl rings in each molecule are coplanar. Types **II** and **III** contain a twisted spacer and the two phenyl rings in each molecule are twisted with respect to each other. Note that the double T-contacts **II** and **III** are interconverted by exchanging the top and bottom molecules; these arrangements are structural isomers. The double face-to-face contact, illustrated

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Scheme 2
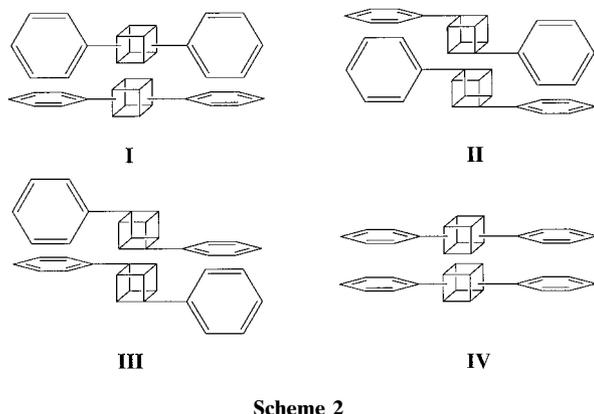
by **IV,** occurs when the two phenyl rings of each molecule interact in a face-to-face fashion. The double T-contacts present in all but a few of the azines we have prepared to date have the conformations shown in **II** and **III.**

We are interested in mixed azines with the structure shown in Scheme 1 because of their promise as nonlinear optical (NLO) materials.[8,9] In order for a crystal to exhibit a NLO response, there are two necessary criteria. First, the crystals must be non-centrosymmetric, or chiral, and this is a requirement for all types of polar effects of crystals (NLO activity, piezo- and pyroelectric, ferroelectric, ferroelastic, and many others). Non-centrosymmetry, however, is readily obtained for organic solids as chiral space groups occur in approximately 20% of organic crystals.[10] The central issue in the aggregation of crystals with macroscopic polarizations is the parallel alignment of the dipole moments of the individual chromophores, and this is a challenge orders of magnitude more complicated than the simple quest for non-centrosymmetry. An important consideration in

IIa   **IIb**

IIc

Scheme 3
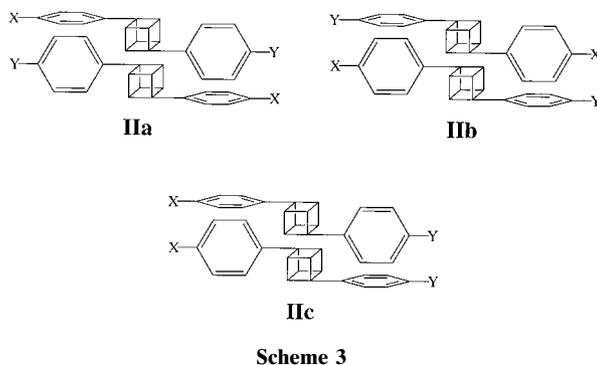
Table 1. Crystal Data and Structure Refinement

Compound	$I-C_6H_4-C(CH_3)=$ $N-N=C(CH_3)-C_6H_4-I$
CCDC deposit no.	CCDC-1003/5652
Color/shape	Colorless/plates
Chemical formula	$C_{16}H_{14}I_2N_2$
Formula Weight	488.09
Temperature, K	173(2)
Crystal system	Orthorhombic
Space Group	*Pbcn*
Unit cell dimensions	$a = 34.5187(19)$ Å
(7364 reflections in full θ	$b = 7.2638(4)$ Å
range)	$c = 6.3736(3)$ Å
Volume, Å³	1598.10(15)
Z	4
Density (calculated), mg/m³	2.029
Absorption coefficient, mm⁻¹	3.928
Diffractometer/scan	Bruker SMART CCD area detector
θ range for data collection, deg	2.36 to 27.20
Reflections measured	8796
Independent/observed reflections	1771 [$R_{int} = 0.0389$]/1613
Data/restraints/parameters	1771/0/91
Extinction Coefficient	None used
Goodness of fit on F^2	1.369
Final R indices [$I > 2s(I)$]	$R1 = 0.0475, wR2 = 0.098$
R indices (all data)	$R1 = 0.0519, wR2 = 0.0994$

choosing chromophores with the general structure shown in Scheme 1 concerns their ability to partake in multiple arene-arene interactions. Our design concept incorporated arene-arene interactions as a means to overcome the electrostatic repulsion of parallel aligned dipole moments. Thus, an understanding of how the substitution patterns on the phenyl rings affect the arene-arene interactions in our systems is a central issue for our studies.[1]

We have previously prepared numerous mixed azines with methoxy, amino and *N,N*-dimethylamino donor groups, and nitro, cyano and halo acceptors.[1,3,4,6,7] Two of these mixed azines crystallize such that their chromophores align in the solid state,[4,6]
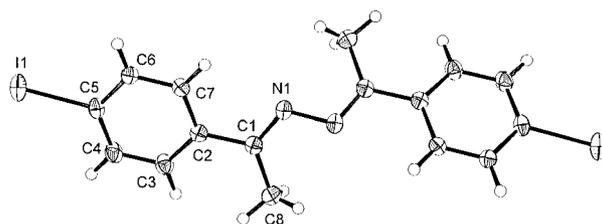
Fig. 1. *ORTEPII* drawing of azine **1.**

Table 2. Atomic Coordinates and Equivalent Isotropic
Displacement Parameters

Atom	x	y	z	U(eq)
I(1)	7125(1)	2761(1)	1180(1)	38(1)
N(1)	5181(1)	3029(7)	−2009(7)	27(1)
C(1)	5465(2)	2503(7)	−3176(8)	23(1)
C(2)	5856(2)	2553(6)	−2205(8)	21(1)
C(3)	6179(2)	1784(8)	−3189(9)	27(1)
C(4)	6542(2)	1862(8)	−2262(9)	28(1)
C(5)	6584(2)	2692(7)	−319(9)	24(1)
C(6)	6266(1)	3430(7)	712(8)	24(1)
C(7)	5906(1)	3367(7)	−227(8)	22(1)
C(8)	5418(2)	1840(10)	−5376(9)	39(2)

however the majority have solid-state lattices where the individual molecules align such that the molecular dipole moments cancel each other. The antiparallel dipole alignment that we observe in most of our crystals allows us to study the intermolecular arene-arene interactions between a donor-substituted phenyl ring and an acceptor-substituted phenyl ring (**IIa** and **IIb** in Scheme 3). However, for NLO activity it is imperative that the molecular dipole moments align, and this would result in intermolecular arene-arene interactions between two donor-substituted phenyl rings and two acceptor-substituted phenyl rings (**IIc** in Scheme 3). Since parallel dipole alignment is extraordinarily difficult to achieve, we have prepared numerous symmetric azines (X═Y in Scheme 1) as a means of investigating the arene-arene interactions between two like-substituted phenyl rings. We have previously reported the crystal structure of the parent azine (X═Y═H (**2**) in Scheme 1), and the crystal structures of the symmetric halogenated azines (X═Y═F (**3**), Cl (**4**) and Br (**5**) in Scheme 1),[1] and in this paper we complete the series with the crystal structure of 4-iodoacetophenone azine, **1.** The crystal structure

of **1** has been extremely elusive because of crystal growth problems.

Experimental

Azine **1** was prepared by first reacting 4-iodo acetophenone with hydrazine hydrate to give 4-iodo acetophenone hydrazone. 4-iodoacetophenone hydrazone was condensed with another molecule of 4-iodoacetophenone to yield **1.** Crystals were obtained from slow diffusion of hexane into a solution of **1** in chloroform. The crystallographic data is given in Table 1 and the fractional coordinates are shown in Table 2.

Results and discussion

The *ORTEP II* diagram of **1** is shown in Fig. 1 and a view of the packing is shown in Figs. 2 and 3. The crystallographic data information for **1** is presented in Tables 1 and 2. The crystal structure of **1** has one independent molecule and it is not planar. Figure 1 reveals that the ─C═N─N═C─ bridge in 4-iodoacetophenone azine assumes a *gauche* conformation ($\tau = 141.8°$). This dihedral angle is somewhat of a surprise when compared to the dihedral angles of **2–5**. The values of τ for azines **2–5** are 138.7° for **2,** 138.0° for **3,** 134.7° for **4** and 124.6° for **5.** This would suggest a τ value for **1** of less than 124°. Instead, the dihedral angle of **1** shows that it is more closely related to **2** and **3**. The dihedral angles relating the twist of the two phenyl rings with respect to the C_{ipso}-imine bond planes in **1,** ϕ_1 and ϕ_2, are 8.0°. Since the N1─N1 bond and the two C2─C1 bonds in **1** are
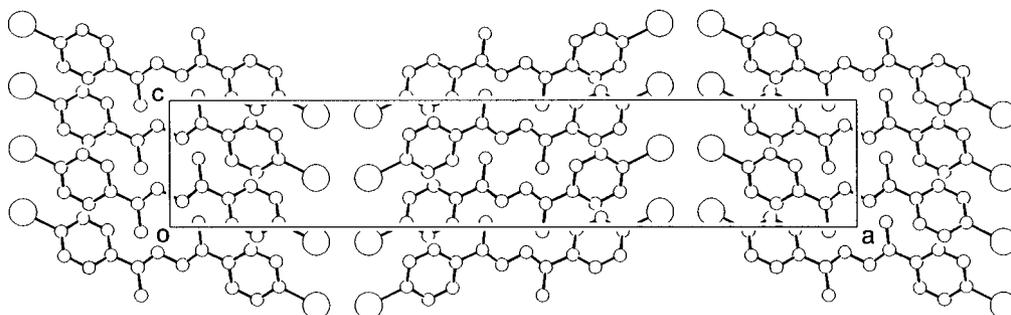
Fig. 2. PLUTO of the crystal packing of azine **1**.
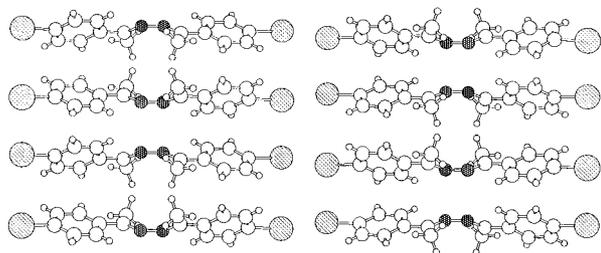
Fig. 3. Chem3D representation of the crystal packing of azine **1,** viewed down the *c*-axis with the *a*-axis on the horizontal and the *b*-axis on the vertical.

almost parallel, the sum of τ' (where $\tau' = 180 - \tau$), 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 $\omega \approx 54.2°$ and leaves the benzenes *gauche.* This does not follow the trend found in the symmetric azines **2–5** where the parent acetophenone azine, **2,** and 4-fluoroaceto-phenone azine, **3,** have $\omega \approx 61.3°$ and 58.8°, respectively, and 4-chloroacetophenone azine, **4,** and 4-bro-moacetophenone azine, **5,** have $\omega \approx 105.1°$ and 103.6°. Thus, the trend for the ω values is the same as for the τ values with azine **1** more closely resembling **2** and **3** than **4** and **5.**

The crystal structure of azine **1** is highly aniso-tropic with the chromophores ordered into repeating layers. Rotation of these layers by 90° with respect to the plane of the page (Fig. 4) reveals that the crystal packing of azine **1** is dominated by double T-contacts. Each azine participates in two unique types of degenerate arene-arene double T-contacts, labeled **A** and **B** in Fig. 4. The distance between the arene rings in the type-**A** double T-contacts is 3.9–4.2 Å; for the type-**B** double T-contacts the distance is 3.6–3.9 Å. Each molecule also partakes in two additional degenerate nearest neighbor interactions that can be described as severely slipped arene-arene double-face-to-face contacts, labeled **C** in Fig. 4. These arene-arene contacts are about a half an Ångström longer than the double T-contacts and thus the double T-contacts are probably the energetically dominant in-termolecular interaction within each layer. It is im-portant to note that the double T-contacts always occur between *P*- and *M*-conformational isomers.[11] Figure 5 shows the *P*- and *M*-isomers involved in the arene-arene double T-contacts **A** and **B**. The designation *P* indicates that the shortest rotation about the N—N bond required to eclipse one phenyl ring with the other is in a clockwise direction. Con-versely, the designation *M* indicates a counterclock-wise rotation. The type-**A** and type-**B** double T-con-tacts are schematically described by **II** and **III** in Scheme 2.

The main difference between the crystal struc-ture of **1** and the parent azine, **2,** and the related symmetrical halogenated azines, **3–5,** relates to the packing between the layers. The layers in azines **2–5**

Fig. 4. Layer of azine **1** viewed down the long molecular axis.
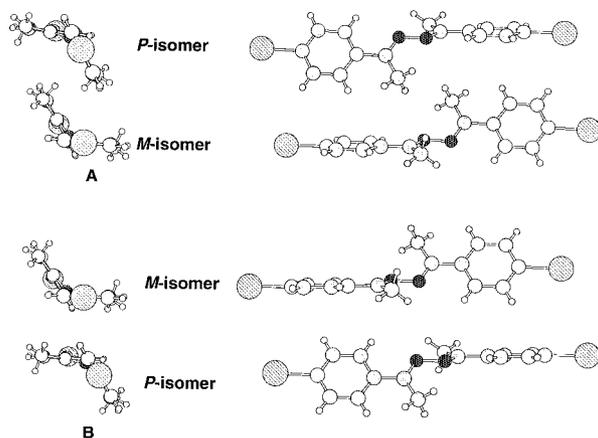
Fig. 5. *P*- and *M*-isomers in the two types of arene-arene double T-contacts in azine **1.**

a = 4.5 Å
b = 5.1 Å
α = 97.1°
β = 76.9°
γ = 88.8°

c = 4.5 Å
d = 4.1 Å
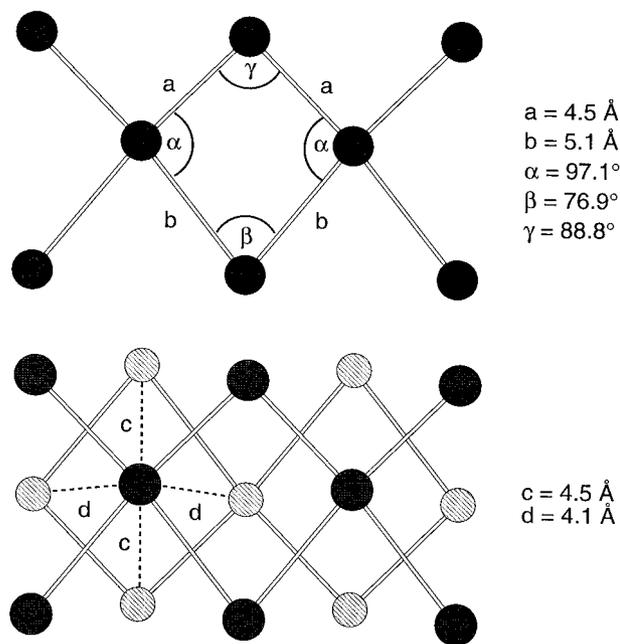
Fig. 6. The top shows the arrangement of iodine atoms at the surface of a layer (Fig. 2 with only the iodine atoms). The iodine atoms are in a quadrilateral kite-shaped motif. The drawing at the bottom shows how the iodine atoms pack between the layers, with the atoms of one layer filling the interstices created by the atoms of the adjacent layer.

all have some degree of interpenetration with adjacent layers, however there is no penetration between the layers in azine **1** (Figs. 2 and 3). The long molecular axes in azine **1** are perfectly parallel within the layers and the azines in different layers deviate from colinearity by approximately 40° (Fig. 2). The interface between the layers is interesting with regards to how the iodine atoms pack. The surface of each layer can be viewed as a plane of iodine atoms arranged in a kite-shaped quadrilateral with two adjacent sides of identical length and three unique angles (Fig. 6 top). The two unique iodine-iodine distances within each layer are 4.5 and 5.1 Å, and these are labeled a and b in Fig. 6. There are also three unique angles relating the iodine atoms within each layer. Angle α is between the two iodine–iodine contacts labeled a and b, angle β is between the two b-type contacts and angle γ is between the two a-type contacts (Fig. 6), and these three angles measure 97.1, 76.9, and 88.8°. The bottom of Fig. 6 describes how the iodine surfaces of two layers pack such that an iodine atom in one layer lies in the square interstices of the kite-shaped arrangement of iodine atoms in the next layer.

The two unique distances relating the iodine atoms of one layer with the iodine atoms of an adjacent layer are $c = 4.5$ and $d = 4.1$ Å (Fig. 6). These short iodine-iodine distances in **1** are just marginally greater than the van der Waals contact distance of 4.0 Å for two iodine atoms,[12] and they are similar to the iodine–iodine close-contacts found in aryltellurium iodides,[13] dialkyldiiodophosphonium iodides,[14] and iron sulfur iodide clusters[15] where the iodine–iodine distances are between 3.8 and 4.5 Å.

The packing motif in **1** is reminiscent of the crystal structures of several mixed azines we reported earlier.[4, 6] In particular, we have synthesized and crystallized two NLO active molecules with the general structure shown in Scheme 1 and X=OMe; Y=Br (6) and X=OMe; Y=Cl (7). The crystal structures of azines **6** and **7** are layered, and they are perfectly dipole parallel-aligned within each layer. However, just like in the case of **1,** the layers in each structure are packed at a 40° angle with respect to each other. This angle results in a decrease in the macroscopic dipole moment of the crystals, and thus a decrease in the NLO activity of the materials. The crystal structure of **1** demonstrates that the deviation from perfect colinear packing is not an asymmetrization effect. Further analysis of the structure of **1** and **6** and **7** are in progress to understand the reason for this deviation from colinearity.

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