

Near-perfect dipole parallel-alignment in the highly anisotropic crystal structure of 4-iodoacetophenone-(4-methoxyphenylethylidene) hydrazone⁽¹⁾

Michael Lewis,⁽²⁾ Charles L. Barnes,⁽²⁾ and Rainer Glaser^{(2)*}

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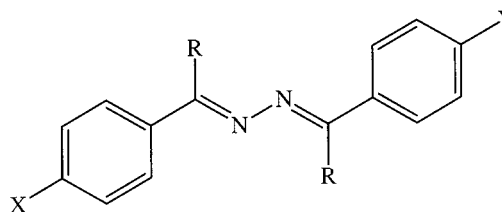
The title compound crystallizes in the space group *Pna*2(1) with cell parameters $a = 6.4606(3)$, $b = 7.2155(3)$ and $c = 33.5878(16)$ Å. The azine shows a *gauche* conformation about the N—N bond and there is an angle of 58.1° between the benzene rings of each azine. This conformation allows for two intermolecular arene–arene T-contacts between pairs of benzene rings. The characteristic structural motif features T-contact formation between like-substituted arene rings and this architecture results in a highly dipole-parallel aligned lattice. All azines are perfectly colinear within each layer and the orientations of the azines in different layers are nearly the same. The surfaces of the layers exhibit a quadrilateral kite-shaped arrangement of I-atoms and of OCH₃-substituents. The layers pack such that the OCH₃—carbon atoms are placed above the interstices between the I-atoms in the adjacent layer.

KEY WORDS: Dipole parallel-alignment; anisotropy; arene–arene contacts; intermolecular interactions; nonlinear optics; azines.

Introduction

We have been investigating the stereochemistry,^{1–4} electronics,^{1,4–6} and crystal packing^{1,4,7–10} 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 are called symmetric if $X = Y$ and unsymmetric, or mixed, if $X \neq Y$. The symmetric³ and unsymmetric^{4,7,8} 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 spacer-connected arene rings of one azine interact with the two arene 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

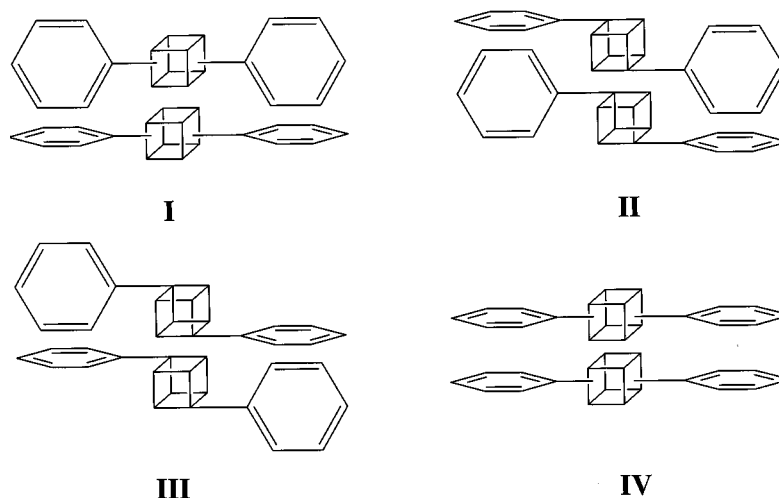


Scheme 1.

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⁽²⁾ Department of Chemistry, University of Missouri–Columbia, Columbia, Missouri 65211. Telephone: (573) 882-0331, Facsimile: (573) 882-2754, E-mail: GlaserR@missouri.edu.

* To whom correspondence should be addressed.



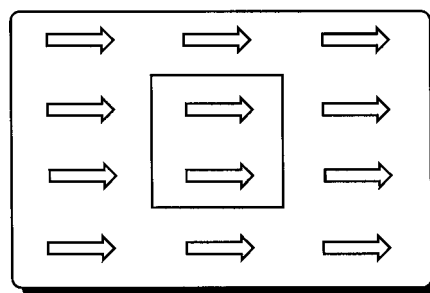
Scheme 2.

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 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 general structure shown in Scheme 1 because of their promise as nonlinear optical (NLO) materials.^{11,12} In order for a crystal to exhibit a NLO response, there are two necessary criterion. First, the crystals must be noncentrosymmetric, 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). Noncentrosymmetry, however, is readily obtained for organic solids as chiral space groups occur in approximately 20% of organic crystals.¹³ The second criterion, and 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 quest for non-centrosymmetry. We have approached the challenge of parallel dipole-alignment in the absence of external fields in a systematic fashion and with a rational design. Scheme 3 helps to illustrate the difficulties in this proposal. Picture (a) in Scheme 1 depicts our goal, the alignment of dipole moments in a crystal lattice. Picture (b) shows what most often

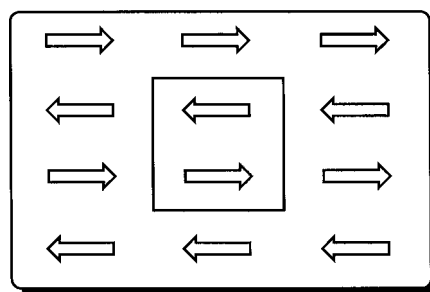
occurs when polar molecules aggregate in the solid phase: the molecules align such that their molecular dipole moments cancel and the dipole moment of the crystal is zero.

Dipole Parallel-Alignment



(a)

Dipole Antiparallel-Alignment



(b)

Scheme 3.

The design concept that we have employed toward preparing dipole parallel-aligned crystals incorporates dipole moment minimization via the use of the azine bridge. Previous studies^{5,14,15} have shown that the azine bridge reduces the molecular dipole moment by acting as a conjugation stopper. A small dipole moment is obviously a key strategic feature in the preparation of dipole parallel-aligned materials because the smaller the molecular dipole moment, the less the electrostatic repulsion. Our design concept also incorporates the use of arene–arene interactions.¹⁶ Numerous theoretical studies have shown that arene–arene contacts are attractive^{17,18} and the energy we gain from these interactions can be used to overcome the electrostatic repulsion of parallel-aligned dipole moments. Following this design concept, we have been successful in preparing dipole parallel-aligned crystals using chromophores with the general structure in Scheme 1. In this paper we report the crystal structure of the dipole parallel-aligned material where $X=\text{OCH}_3$ and $Y=\text{I}$ (**1**). We have previously reported the crystal structures where $X=\text{OCH}_3$ and $Y=\text{Br}$ (**2**)⁴ or Cl (**3**).⁹ Comparisons will be drawn between the crystal structure of **1** and the crystal structure of the symmetric iodo-substituted crystal structure, **4** (Scheme 1, $X=Y=\text{I}$)¹⁰ and the symmetric methoxy-substituted crystal structure, **5** (Scheme 1, $X=Y=\text{OCH}_3$)³ with attention to the packing between layers.

Experimental

Azine **1** was prepared by first reacting 4-methoxyacetophenone with hydrazine hydrate to give 4-methoxyacetophenone hydrazone. 4-Methoxyacetophenone hydrazone was condensed with 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 $-\text{C}=\text{N}-\text{N}=\text{C}-$ bridge in **1** assumes a *gauche* conformation ($\tau = 144.3^\circ$). The τ angle for **1** is

Table 1. Crystal Data and Structure Refinement of **1**

Compound	$\text{I}-\text{C}_6\text{H}_4-\text{C}(\text{CH}_3)=\text{N}=\text{N}=\text{C}(\text{CH}_3)-\text{C}_6\text{H}_4-\text{OCH}_3$
CCDC deposit no.	CCDC-1003/5909
Color/shape	Yellow/plates
Chemical formula	$\text{C}_{17}\text{H}_{17}\text{IN}_2\text{O}$
Formula weight	392.23
Temperature, K	173(2)
Crystal system	Orthorhombic
Space group	<i>Pna</i> 2(1)
Unit cell dimensions	$a = 6.4606(3) \text{ \AA}$
(8793 reflections in full θ range)	$b = 7.2155(3) \text{ \AA}$
Volume, $\text{\AA}^3$	$c = 33.5878(16) \text{ \AA}$
<i>Z</i>	1565.74(12)
Density (calculated), mg/mm^3	4
Absorption coefficient, mm^{-1}	1.664
Diffractometer/scan	2.046
θ range for data collection, deg	Bruker SMART CCD area detector
Reflections measured	2.43 to 27.11
Independent/observed reflections	8793
Data/restraints/parameters	3428 [$R_{\text{int}} = 0.0235$]/3428
Extinction coefficient	3428/1/194
Absolute structure parameter	None used
Goodness of fit on F^2	0.280(18)
Final <i>R</i> indices [$I > 2s(I)$]	1.135
<i>R</i> indices (all data)	$R1 = 0.0223, wR2 = 0.0533$
	$R1 = 0.0237, wR2 = 0.0538$

Table 2. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for **1**

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq) ^a
I(1)	1791(1)	338(1)	0(1)	32(1)
O(1)	−4452(4)	−166(3)	−4219(1)	29(1)
N(1)	−1258(4)	538(4)	−2008(1)	26(1)
C(1)	−2426(5)	6(4)	−1720(1)	22(1)
N(2)	−2206(5)	500(4)	−2382(1)	26(1)
C(2)	−1467(5)	56(4)	−1314(1)	23(1)
C(3)	−2473(5)	−720(4)	−982(1)	27(1)
C(4)	−1548(5)	−645(4)	−606(1)	30(1)
C(5)	361(5)	192(4)	−558(1)	26(1)
C(6)	1390(5)	946(5)	−887(1)	26(1)
C(7)	477(5)	866(4)	−1260(1)	24(1)
C(8)	−4610(6)	−662(6)	−1769(1)	40(1)
C(9)	−989(5)	34(4)	−2673(1)	22(1)
C(10)	−1903(5)	24(4)	−3076(1)	22(1)
C(11)	−926(5)	−867(4)	−3395(1)	23(1)
C(12)	−1818(5)	−894(5)	−3772(1)	26(1)
C(13)	−3709(5)	−33(4)	−3838(1)	21(1)
C(14)	−4705(5)	881(4)	−3525(1)	23(1)
C(15)	−3808(5)	881(4)	−3148(1)	22(1)
C(16)	1225(7)	−538(6)	−2614(1)	35(1)
C(17)	−6390(5)	619(5)	−4301(1)	33(1)

^a *U*(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

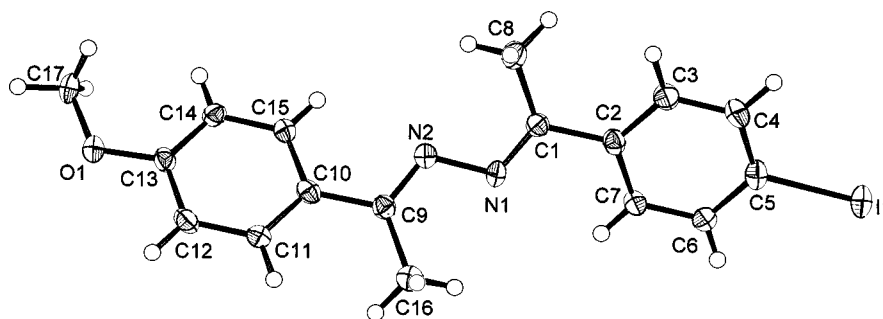


Fig. 1. ORTEP drawing of azine **1**.

about 10° smaller than the respective angles for **2** ($\tau = 135.8^\circ$) and **3** ($\tau = 134.7^\circ$). The dihedral angles relating the twist of the two phenyl rings with respect to the C_{ipso} -imine bond planes in **1**, ϕ_1 for the methoxy-substituted phenyl ring and ϕ_2 for the iodo-substituted phenyl ring, are 14.4° and 8.0° , respectively. Since the N1—N2, C1—C2 and C9—C10 bonds in **1** are 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 $\omega \approx 58.1^\circ$ and leaves the benzenes *gauche*. As was the case for the dihedral angle τ , the ω angle for **1** is smaller than the respective angle for **2** ($\omega = 64.2^\circ$) and **3** ($\omega = 64.0^\circ$). The fact that the dihedral and twist angles of the iodo-substituted structure differ from the respective angles of the chloro- and bromo-substituted analogs is not surprising in light of an earlier analysis of the symmetric 4-iodoacetophenone azine, **4**. The τ and ω angles of **4** differ substantially from the same angles in the symmetric 4-chloro- and 4-bromoacetophenone azines.¹⁰

Our previous investigations into the N—N *gauche* conformation of mixed azines showed that the azine bridge is essentially a conjugation stopper. Crystallographic and *ab initio* studies^{5,9} showed that the bond distances and populations of one phenyl ring are virtually unaffected by the substitution pattern on the other phenyl ring. Likewise, electrochemical studies^{14,15} have also shown that the azine bridge impedes conjugation. The N—N *gauche* conformation in **1** would suggest that the azine bridge is once again acting as a conjugation stopper. If this is true then we would expect little contribution from resonance form **1a** (Scheme 4) in the ground state structure of **1**.

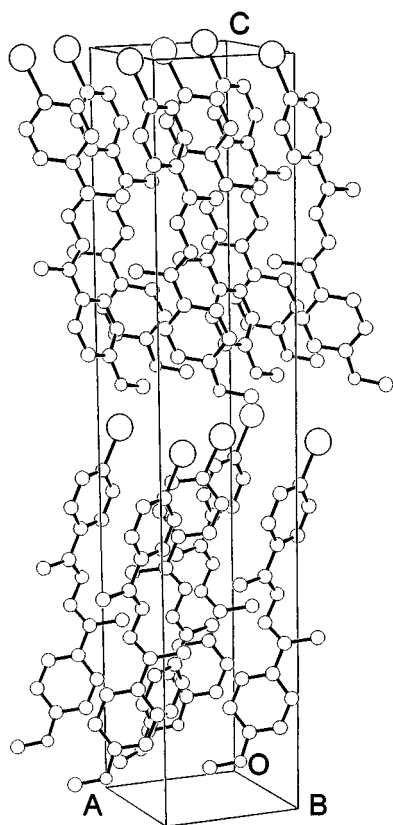
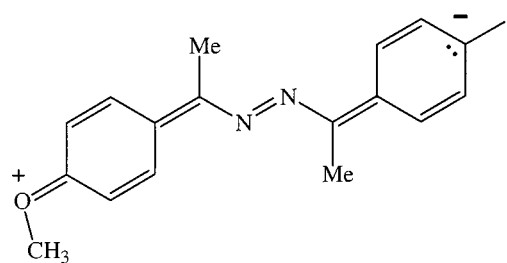


Fig. 2. PLUTO drawing of the crystal packing of azine **1**.



1a

Scheme 4.

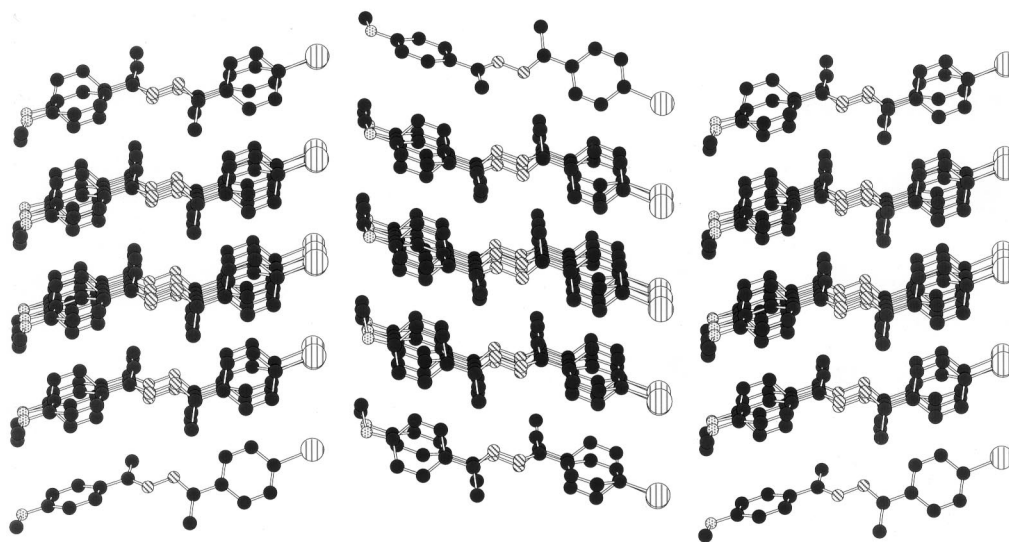


Fig. 3. Chem3D representation of the crystal packing of azine **1**, viewed down the diagonal of the *ab*-plane with the *c*-axis on the horizontal.

The importance of resonance form **1a** should be manifest through a structural comparison of mixed azine **1** with the symmetrical azines 4-iodoacetophenone azine (**4**)¹⁰ and 4-methoxyacetophenone azine (**5**).³ If there existed a substantial decrease in the C(2)—C(1) and N(1)—N(2) bond lengths, and an increase in the I(1)—C(5) and C(1)=N(2) bond lengths in **1** with respect to **4**, then this would suggest that conjugation plays a role in the ground state of **1**. Likewise, a decrease in the C(13)—O(1), C(10)—C(9) and N(1)—N(2) bond lengths, and an increase in the C(9)=N(2) bond length in **1** with respect to **5** would also suggest that conjugation plays a role in the ground state of **1**. Table 3 shows the comparisons between the four pertinent bond lengths for **1**

Table 3. Comparisons of Bond Distances in **1** and **4** and in **1** and **5** to Determine the Extent of Conjugation in **1**^a

Bond	1 (Å)	4 (Å)	5 (Å)
I(1)—C(5)	2.09	2.10	—
C(1)=N(1)	1.29	1.29	—
C(2)—C(1)	1.50	1.49	—
N(1)—N(2)	1.40	1.40	—
C(13)—O(1)	1.37	—	1.36
C(9)=N(2)	1.30	—	1.28
C(9)—C(10)	1.48	—	1.48
N(1)—N(2)	1.40	—	1.41

^aThe esd values for molecules **1**, **4**, and **5** are all to the third decimal place. Our comparisons all involve bond distances to the second decimal place, and thus the esd values are not pertinent.

and **4** and for **1** and **5**. The I(1)—C(5), C(1)=N(1), C(2)—C(1) and N(1)—N(2) bond lengths in **1** are all approximately the same as those in azine **4**. Similarly, the C(13)—O(1), C(9)=N(2), C(9)—C(10) and N(1)—N(2) bond lengths in **1** are all approximately the same as those in azine **5**. In all cases, deviations of no greater than 0.02 Å exist between the pertinent bond lengths in azines **1** and **4** and between those in azines **1** and **5**. Moreover, the directions of these small changes are not consistent with contribution from resonance form **1a** to the ground state of **1**. Thus, the azine bridge in **1** is operating as a conjugation stopper. The half of azine **1** with the methoxy-substituted phenyl ring is impervious to the substituent located on the phenyl ring in the other half, and the same statement can be made about the half of azine **1** with the iodo-substituted phenyl ring.

The B3LYP/6-31G* calculated dipole moment of **1** is 3.3 Debye. We have previously studied the effects of azine conformation on the molecular dipole moment.⁵ In this report we studied azines with the general formula shown in Scheme 1 where the donor substituent was OCH₃ and the acceptors were F, Cl, Br, CN and NO₂. The ground state dipole moments were calculated for the optimized *gauche* conformations and the planar structures. The dipole moments all fell in the range 3–7 D and for each structure the effect of conformation was less than 0.12 D. The same would be expected for **1**.

The crystal structure of azine **1** is highly anisotropic with the chromophores ordered into

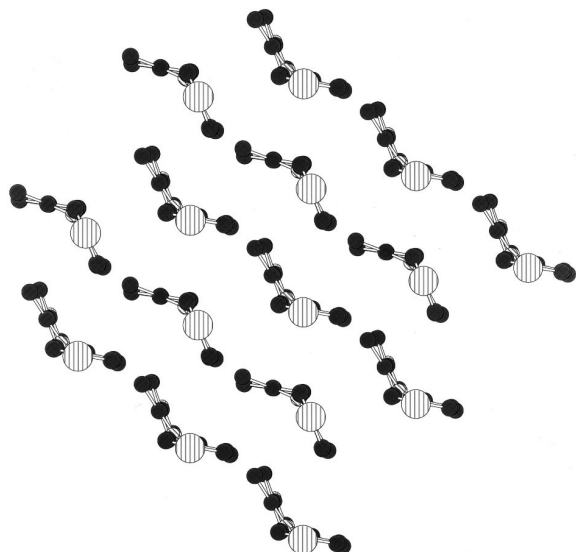


Fig. 4. Layer of azine **1** viewed down the long molecular axis.

repeating layers (Fig. 3). Rotation of these layers by 90° with respect to the plane of the page (Fig. 4) reveals that the predominant intermolecular interactions within each layer are the arene–arene double T-contacts (Fig. 5) of the types described by **II** and **III** in Scheme 2. The molecules pack within the lay-

ers such that the arene–arene T-contacts always occur between two methoxy-substituted phenyl rings or two iodo-substituted phenyl rings, but never between a methoxy- and an iodo-substituted ring. The distance between the iodo-substituted arene rings in the type-**II** double T-contact is 3.8–4.2 Å. The methoxy-substituted arene rings in **II** are separated by 3.6–4.1 Å. For the type-**III** double T-contacts, the distance between the iodo-substituted arene rings is 3.5–4.0 Å and the distance between the methoxy-substituted arene rings is 3.6–4.1 Å. It is important to note that the double T-contacts always occur between *P*- and *M*-conformational isomers.¹⁹ Figure 5 shows the *P*- and *M*-isomers involved in the arene–arene double T-contacts **II** and **III**. 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. Conversely, the designation *M* indicates a counterclockwise rotation.

Since the arene–arene T-contacts always occur between like substituted phenyl rings, each layer in the crystal structure of **1** forms a two-dimensional array of perfectly dipole parallel-aligned chromophores. If one achieves dipole parallel-alignment within a two-dimensional layer, then electrostatics dictate that the third dimension *must* also be dipole parallel-aligned. This is realized in the crystal structure of **1**; however, the packing between the layers

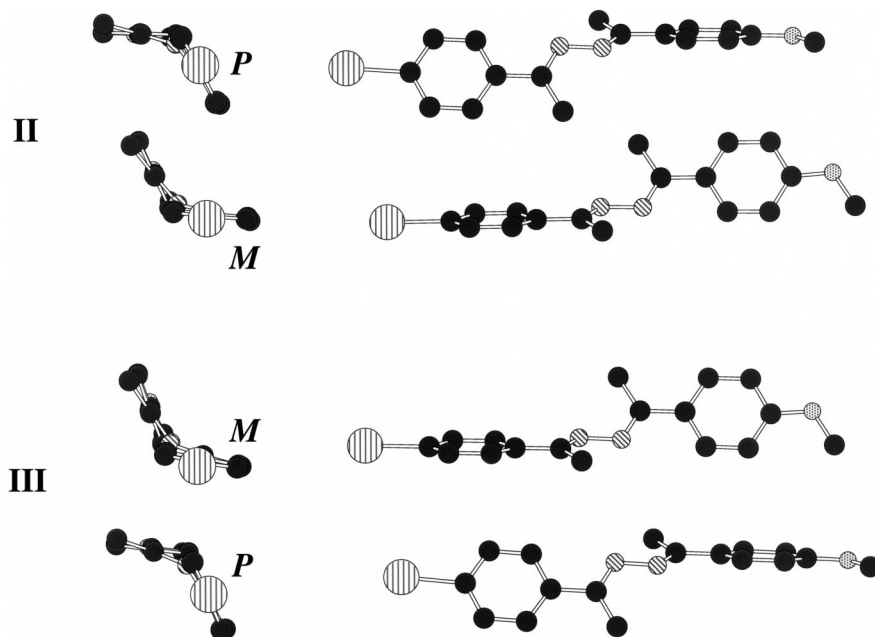


Fig. 5. *P*- and *M*-isomers in the two types of arene–arene double T-contacts in azine **1**.

is not quite the perfect scenario depicted in Scheme 3a. The packing between the layers deviates from perfect dipole parallel-alignment by an angle of approximately 35° . Taking into account this angle between the layers, the crystal structure of **1** is 95% dipole parallel-aligned.

The azine layers in the crystal structure of **1** are terminated by surfaces containing iodine atoms and methoxy substituents. The interface between the layers is interesting with regards to how the iodine atoms of one layer pack with the methoxy substituents of the neighboring layer. The iodine surface 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 are $a = 4.5$ and $b = 5.2$ Å. 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, top), and these three angles measure 95.7° , 76.5° , and 92.0° . The iodine surface in **1** is very similar to the iodine surface in **4**.¹⁰ The a and b distances in **4** are 4.5 and 5.1 Å, respectively, and the α , β and γ angles are 97.1° , 76.9° , and 88.8° . Thus, asymmetrization does not significantly affect the arrangement of the iodine surface.

The methoxy surface can be viewed in a similar fashion, where the carbon atoms are arranged in a kite-shaped quadrilateral (Fig. 6, middle). The oxygen atoms also form a kite-shaped quadrilateral, but

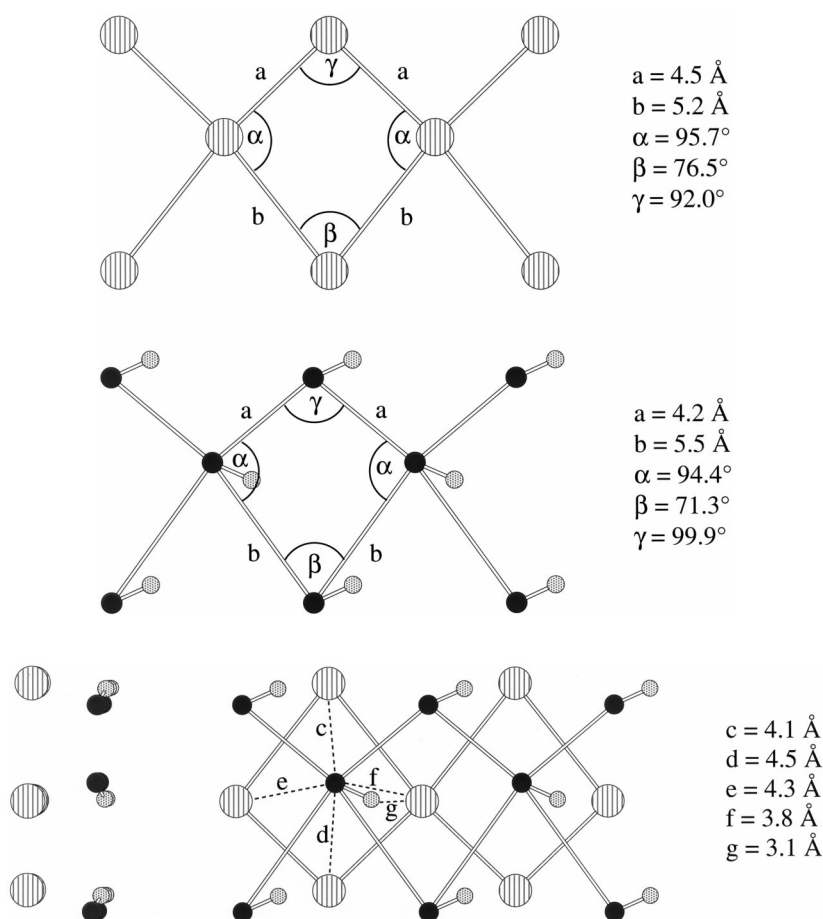


Fig. 6. The top shows the arrangement of iodine atoms at the surface of a layer and the middle picture shows the arrangement of the methoxy substituents. The iodine atoms and the methoxy substituents are in a quadrilateral kite-shaped motif. The drawing at the bottom shows how the two surfaces pack, with the carbon atoms of the methoxy substituents lying in the interstices created by the iodine atoms.

it is the carbon atoms that pack in the interstices of the iodine surface and thus we will focus on the carbon atom pattern. The *a* and *b* distances for the quadrilateral formed by the carbon atoms are 4.2 Å and 5.5 Å and the angles are $\alpha = 94.4^\circ$, $\beta = 71.3^\circ$, $\gamma = 99.9^\circ$ (Fig. 6, middle).

The interfacial packing of the iodine and methoxy surfaces is described in the bottom picture of Fig. 6. The carbon atoms of the methoxy groups lie in the square interstices of the kite-shaped arrangement of iodine atoms in the next layer. One of the methoxy hydrogen atoms points straight into the center of the interstice of the iodine atoms. The distances between this hydrogen atom and the four iodine atoms are between 3.5 and 3.9 Å and this is well outside the van der Waals distance of 3.3 Å.²⁰ The four distances relating the methoxy carbon atoms of one layer with the iodine atoms of an adjacent layer are *c* = 4.1 Å, *d* = 4.5 Å, *e* = 4.3 Å and *f* = 3.8 Å (Fig. 6, bottom). This interlayer packing motif results in very short contacts between every methoxy oxygen atom and one iodine atom. This oxygen-iodine distance is 3.1 Å and it is considerably shorter than the van der Waals contact distance of 3.4 Å for oxygen and iodine.²⁰

The short oxygen-iodine packing between the layers in the crystal structure of **1** provides an explanation as to why we have had difficulty crystallizing molecules with the general structure in Scheme 1 with methoxy donors and fluorine and cyano acceptors. Highly polarizable substituents, such as bromine and iodine, can better withstand being in close contact with an oxygen atom than the highly electronegative, relatively nonpolarizable fluorine and cyano groups. The analysis described in the present paper suggests two approaches toward improvement of the interlayer interaction in dipole parallel-aligned organic crystals. Our design concept might benefit from the incorporation of more polarizable acceptor groups

and the use of donors that avoid the occurrence of any short intermolecular donor-acceptor interactions.

Acknowledgments

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