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The crystal structure of the title mixed azine, C_{17}H_{17}ClN_{2}O, contains four independent molecules, A–D, and molecule B is disordered. All four molecules have an N–N gauche conformation, with C–N–N–C torsion angles of 136.5 (4), 137.0 (4), −134.7 (4) and −134.7 (4)°, respectively. The phenyl rings are also somewhat twisted with respect to the plane defined by C_{ipso} and the imine bond. On average, the combined effect of these twists results in an angle of 64.7° between the best planes of the two phenyl rings. Arene–arene double T-contacts are the dominant intermolecular interaction. The methoxy-substituted phenyl ring of one azine molecule interacts to form a T-contact with the methoxy-substituted phenyl ring of an adjacent molecule and, similarly, two chloro-substituted phenyl rings of neighboring molecules interact to form another T-contact. The only exception is for molecule B, for which the disorder leads to the formation of T-contacts between methoxy- and chloro-substituted phenyl rings. The prevailing structural motif of T-contact formation between like-substituted arene rings results in a highly dipole-parallel-aligned crystal structure.

Comment

We have been investigating the stereochemistry (Glaser et al., 1993, 1995; Chen et al., 1995), electronics (Glaser et al., 1993; Chen et al., 1995; Glaser & Chen, 1998) and crystal packing of symmetric and unsymmetric azines. An azine is the condensation product of 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 $X$ equals $Y$ and unsymmetric or mixed if $X$ does not equal $Y$. All of the mixed azines that we have investigated [$R = Me, X = OCH_3, Y = Br, CN$ or NO$_2$ (Glaser et al., 1995); $R = Me, X = NH_2, Y = F$ (Lewis et al., 1998)] 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 nearly orthogonal and this allows for the arene–arene double T-contact throughout the crystal structures of the previously studied mixed azines. A T-contact describes the edge-to-face interaction between two phenyl rings. Such arrangements are typically characterized by distances of 3.5–5.0 Å between the midpoints of the benzene rings (Hobza et al., 1994). 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–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 structural isomers and differ only in the choice of the benzene edges used in the double T-contact. 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 of the mixed azines that we have prepared to date have the conformations shown in II and III, with inter-ring distances of 3.5–5.0 Å.

We are interested in mixed azines with the structure shown in Scheme 1 because of their promise as non-linear optical (NLO) materials. In order for a crystal to exhibit an NLO response, there are two necessary conditions. 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 pyroelectricity, ferroelectricity, ferroelasticity and many others). Non-centrosymmetry, in fact, occurs in approximately 20% of organic crystals (Sakamoto, 1997). The second condition, 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 greater than the simple quest for non-centrosymmetry. We have previously...
prepared 4-bromoacetophenone [1-(4-methoxyphenyl)ethylidene]hydrazone, (2) ($X = \text{OCH}_3, Y = \text{Br}, R = \text{CH}_3$; Chen et al., 1995). The crystal structure of (2) is highly anisotropic, with the long axes of all of the azine molecules pointing in the same direction, and moreover it has a high degree of dipole parallel alignment, with all of the dipole moments also pointing in the same direction. In this report, we discuss the crystal structure of 4-chloroacetophenone [1-(4-methoxyphenyl)ethylidene]hydrazone, (1) ($X = \text{OCH}_3, Y = \text{Cl}, R = \text{CH}_3$). As in the case of (2), azine (1) is an extremely anisotropic material, albeit with a somewhat lower degree of dipole parallel alignment due to the disorder of molecules B.

Mixed azine (1) is the condensation product of a para-methoxyacetophenone molecule, a para-chloroacetophenone molecule and hydrazine. The bromine analog (2) was prepared previously and its crystal structure reported by Chen et al. (1995). The crystal structure of azine (2) is monoclinic with $P2_1$ symmetry [$a = 7.766$, $b = 31.949$ and $c = 6.339$ Å, $\beta = 95.38^\circ$ and $Z = 4$]. The similarity of the cell dimensions with those of azine (1) led us to assume that (1) and (2) were isostructural. Refinement of (1) in $P2_1$ gave a model in which one of the two independent molecules was disordered and the refinement converged to $R = 13\%$. The merging $R$ factor in the monoclinic setting, however, was 10% and an unconstrained refinement of the cell dimensions gave $\alpha$ and $\gamma$ angles that deviated significantly from $90^\circ$. Refinement of the structure in the triclinic setting in space group $P1$ gave an $R$ factor of 5%. In the triclinic structure, there are four independent molecules in the unit cell (Fig. 1, molecules $A$–$D$) and the disorder is limited to only one molecule ($B$). Because of the deviation of unit-cell parameters from monoclinic and because the disorder is more localized, the crystal structure of (1) is better described in the triclinic setting.

The crystal structure of (1) is layered (Fig. 2), with molecules $A$ and $C$ always residing in one layer and molecules $B$ and $D$ in the other. Molecule $B$ is disordered such that in 43% of the molecules the chloro group is pointing in the same direction as the chloro group of molecule $D$. For the other 57% of the molecules, the chloro group is pointing in the opposite direction. The layers in (1) are at an angle of approximately 35° with respect to each other. The conformation about the azine bridge in (1) (Fig. 1) is $N$–$N$ gauche for all four independent molecules. The torsion angles $C1$–$N1$–$N2$–$C9$ are 136.5 (4), 137.0 (4), $-134.7$ (4) and $-134.7$ (4)° for molecules $A$–$D$, respectively. Our previous electronic investigations into the $N$–$N$ gauche conformation of mixed azines showed that the azine bridge is essentially a conjugation stopper (Glaser & Chen, 1998). Crystallographic and $ab$ initio studies showed that the bond distances and populations of one phenyl ring are virtually unaffected by the substitution pattern on the other phenyl ring. 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) in the ground-state structure of (1).

The importance of resonance form (1a) should be manifest through a structural comparison of mixed azine (1) with the symmetrical azines 4-methoxyacetophenone azine, (3) ($R = \text{CH}_3, X = Y = \text{OMe}$; Glaser et al., 1995), and 4-chloroacetophenone azine, (4) ($R = \text{CH}_3, X = Y = \text{Cl}$; Glaser et al., 1993). If there existed a substantial decrease in the $C13$–$O1$, $C10$–$C9$ and $N2$–$N1$ bond lengths and a significant increase in the $C9$, $N2$ bond length in (1) with respect to (3), then this would
suggest that conjugation played a role in the ground state of (1). Likewise, a decrease in the C2—C1 and N1—N2 bond lengths and an increase in the C11—C5 and C1=N2 bond lengths in (1) with respect to (4) would also suggest that conjugation plays a significant role in the ground state of (1). We compared the four pertinent bond lengths for (1) and (3) (C13—O1, C9—N2, C9—C10 and N1—N2) and for (1) and (4) (C1—C5, C1—N1, C2—C1 and N1—N2), and in all cases the deviations are no greater than 0.02 Å. 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 stopper. The half of azine (1) with the methoxy-substituted phenyl ring in azine molecule A is always involved in a T-contact with the chloro-substituted ring of an adjacent azine molecule B. Likewise, the chloro-substituted phenyl ring of azine molecule A is always involved in a T-contact with a chloro-substituted phenyl ring of a neighboring azine molecule C. In this manner, each azine molecule A takes part in two type-II double T-contacts and one type-III double T-contact with neighboring azine C molecules. A similar motif is found for the layer containing molecules B and D, except that molecule B is disordered. Thus, in 43% of cases, the methoxy-substituted phenyl ring in azine molecule B is involved in a T-contact with the chloro-substituted phenyl ring of an adjacent azine molecule D. In the other 57% of cases, it is involved in a T-contact with the chloro-substituted phenyl ring of an adjacent azine molecule D. As was the case for the layer containing azine molecules A and C, each azine molecule in the layer containing molecules B and D takes part in two type-II double T-contacts and one type-III double T-contact.

The crystal structure of (1) has a high degree of dipole parallel alignment. Ab initio molecular orbital calculations show that the vectors of the dipole moments of molecules A–D are all essentially along the long axis of each azine molecule. Furthermore, the direction of the N—N bond in each azine is also collinear with the long axis of the molecule and all of the N—N bonds are almost perfectly parallel. Thus, within the layer containing molecules A and C, the degree of dipole parallel alignment is essentially complete. The disorder in molecule B detracts somewhat from the dipole parallel alignment of the layer containing molecules B and D. After taking into account the disorder at molecule B, the degree of dipole parallel alignment in the crystal structure of (1) is approximately 71.5% that of (2). The crystal structure of (1), however, promises to be a better candidate for understanding the electronic factors involved in dipole parallel alignment. Why is there disorder and why is the disorder so highly ‘organized’ that it affects only molecules B? Molecule B exists in a crystal environment that is at the junction between dipole parallel alignment and dipole antiparallel alignment, and we are currently studying this phenomenon with ab initio molecular orbital theory.

**Experimental**

Diethyl phosphite and hydrazine hydrate were reacted in a solution of tetrachloromethane, dichloromethane and potassium carbonate with a catalytic amount of triethylbenzylammonium chloride to give diethyl phosphite-(4-methoxyphenylethylidene)hydrazone, which was then coupled with para-methoxyacetophenone in benzene to give diethylphosphine-(4-methoxyphenylethylidene)hydrazone. The crystal structure of (1) was obtained by slow diffusion of hexane into a solution of (1) in chloroform.
Refinement

$R = 0.05$
$wR = 0.13$
$S = 1.108$

7704 reflections
760 parameters
H-atom parameters constrained

$$w = 1/\left[\sigma^2(F_o^2) + (0.0378P)^2 + 1.7102P\right]$$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta P)_{\text{max}} = 0.004$
$P_{\text{max}} = 0.32 \text{ e Å}^{-3}$
$P_{\text{min}} = -0.30 \text{ e Å}^{-3}$

Absolute structure: Flack (1983)
Flack parameter = 0.02 (7)

The positional parameters of the disordered Cl and methoxy groups were not constrained or restrained during refinement, leading to less than ideal geometry for these moieties. In particular, the C—Cl bond distances are longer than those in the ordered molecules. H atoms were placed in calculated positions with C—H = 0.95 Å (0.98 Å for methyl H) and $U_{iso} = 1.2U_{eq}(C)$.

Table 1
Selected geometric parameters (Å, °) in molecules A–D of (1).

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<th></th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
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Data collection: SMART-NT (Bruker, 1998); cell refinement: SMART-NT; data reduction: SMART-NT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: ORTEPII (Johnson, 1976); software used to prepare material for publication: SHELXL97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1211). Services for accessing these data are described at the back of the journal.

References