$w = 1/[\sigma^2(F_o) + 0.00302|F_o|^2]$

$(\Delta/\sigma)_{max} = 0.006$

Scattering factors from *International Tables for Crystallography* (Vol. C)

4-Methoxybenzaldehyde pentafluorophenylmethylidenehydrazone†

MICHAEL LEWIS,[a] CHARLES L. BARNES,[a] BRUCE A. HATHAWAY[b] AND RAINER GLASER[a]

[a]Department of Chemistry, University of Missouri, Columbia, Missouri 65211, USA, and [b]Department of Chemistry, Southeast Missouri State University, Cape Girardeau, Missouri 63701, USA. E-mail: glaserr@missouri.edu

Table 1. *Selected geometric parameters (Å, °)*

O1—C7	1.227 (2)	C2—C7	1.508 (2)
N1—C1	1.332 (2)	C3—C4	1.381 (2)
N1—C5	1.345 (2)	C4—C5	1.396 (2)
N2—C7	1.354 (2)	C5—C6	1.535 (2)
N2—C8	1.451 (2)	C6—C10	1.524 (3)
N2—C9	1.462 (2)	C6—C11	1.516 (3)
C1—C2	1.391 (2)	C6—C12	1.518 (3)
C2—C3	1.388 (2)		
C1—N1—C5	118.0 (1)	N1—C5—C6	115.2 (1)
C7—N2—C8	125.9 (1)	C4—C5—C6	123.5 (1)
C7—N2—C9	119.1 (1)	C5—C6—C10	111.6 (1)
C8—N2—C9	115.0 (1)	C5—C6—C11	108.3 (1)
N1—C1—C2	124.6 (1)	C5—C6—C12	109.1 (1)
C1—C2—C3	117.0 (1)	C10—C6—C11	108.0 (2)
C1—C2—C7	117.6 (1)	C10—C6—C12	109.1 (2)
C3—C2—C7	125.2 (1)	C11—C6—C12	110.8 (2)
C2—C3—C4	119.3 (1)	O1—C7—N2	122.6 (1)
C3—C4—C5	119.8 (1)	O1—C7—C2	118.6 (1)
N1—C5—C4	121.3 (1)	N2—C7—C2	118.8 (1)

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1994). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1995). Program(s) used to solve structure: *SAPI91* (Fan, 1991). Program(s) used to refine structure: *TEXSAN*. Software used to prepare material for publication: *TEXSAN*.

References

Donkersloot, M. C. A. & Buck, H. M. (1981). *J. Am. Chem. Soc.* **103**, 6554–6558.

Fan, H.-F. (1991). *SAPI91*. Structure Analysis Programs with Intelligent Control. Rigaku Corporation, Tokyo, Japan.

Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Mikata, Y. (1997). *Acta Cryst.* C53, 1486–1488.

Molecular Structure Corporation (1994). *MSC/AFC Diffractometer Control Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

Molecular Structure Corporation (1995). *TEXSAN. Single Crystal Structure Analysis Software*. Version 1.7. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A24, 351–359.

Ohno, A., Tsutsumi, A., Kawai, Y., Yamazaki, N., Mikata, Y. & Okamura, M. (1994). *J. Am. Chem. Soc.* **116**, 8133–8137.

Okamura, M., Mikata, Y., Yamazaki, N., Tsutsumi, A. & Ohno, A. (1993). *Bull. Chem. Soc. Jpn*, **66**, 1197–1203.

Zachariasen, W. H. (1967). *Acta Cryst.* **23**, 558–564.

Abstract

The crystal structure of the mixed azine $C_{15}H_9F_5N_2O$ is described. The molecule has a high degree of planarity. The two phenyl rings deviate from perfect planarity by less than 2° and the dihedral angles between the *ipso*-C atoms and the azine bridge also show a minute deviation from planarity of less than 2°. The only dihedral angle that indicates any significant twisting is the dihedral angle about the azine bridge [C1—N1—N2—C8 174.8 (6)°], and even this one is relatively small. Face-to-face arene–arene contacts are the dominant intermolecular interactions. There are double face-to-face contacts in which the two phenyl rings of one mixed azine interact with the two phenyl rings of another mixed azine. There are also single face-to-face contacts where one phenyl ring of one mixed azine interacts with a phenyl ring of another mixed azine. In the double face-to-face arene–arene contacts, the pentafluorinated phenyl ring of one mixed azine always interacts with the methoxy-substituted phenyl ring of another mixed azine. In the single face-to-face arene–arene contacts, the interactions are always between two pentafluorinated phenyl rings or two methoxy-substituted phenyl rings.
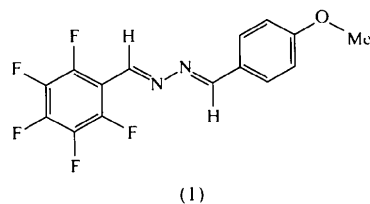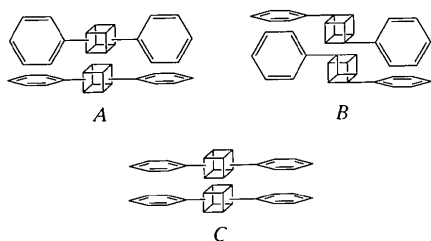
Comment

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 (Glaser *et al.*, 1993; Chen *et al.*, 1995; Lewis *et al.*, 1998) of symmetric and unsymmetric azines. An azine is the condensation product between
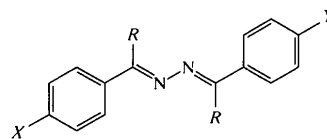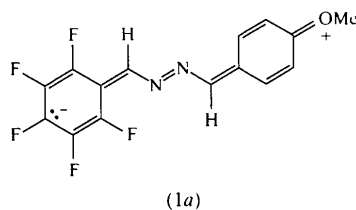

† Part 10 in the series 'Stereochemistry and Stereoelectronics of Azines'. For part 9, see Hathaway *et al.* (1998).

two carbonyl molecules and hydrazine. The azines that we have studied have the general structure shown in the first scheme above, and they are called symmetric if X equals Y and unsymmetric, or mixed, if X does not equal Y. The conformation about the azine bridge in our previously studied azines was either N—N *trans* or N—N *gauche*, depending on the substituent. 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)] do not show this dichotomy, and they 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 arene–arene contact throughout the lattices of the previously studied mixed azines. A double T-contact occurs when the two phenyl rings of one mixed azine interact with the two phenyl rings of another mixed azine to form two intermolecular arene–arene T-contacts. Three types of double arene–arene contacts are illustrated below; *A* and *B* are both double T-contacts and *C* is a double face-to-face contact. Type *A* has a planar spacer and the two phenyl rings of one molecule act as the 'head' and the two phenyl rings of the adjacent molecule act as the vertices for the two T-contacts. Type *B* contains a twisted spacer and one of the phenyl rings in each molecule acts as the 'head' or vertex, respectively, for the T-contacts. The double face-to-face contact, illustrated by *C*, 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 conformation shown in *B*.

A   *B*

C

In this context, we are studying the quadrupole–quadrupole interactions between the phenyl rings involved in the double arene–arene contacts. One method of varying the quadrupole moment of an aromatic species is through fluorination. The Q_{zz} component of the quadrupole moment of hexafluorobenzene is 50% greater than that of benzene (Hathaway *et al.*, 1998). Thus, we are interested in the stereoelectronic and crystal-packing effects of fluorination on the azines shown, and in this report we describe the crystal structure of 4-methoxybenzaldehyde pentafluorophenyl-methylidenehydrazone, (1).

Mixed azine (1) is the condensation product between a *para*-methoxy benzaldehyde molecule, a pentafluori-

(1)

nated benzaldehyde molecule, and hydrazine. The conformation about the azine bridge in (1) (Fig. 1) is almost perfectly N—N *trans* [C1—N1—N2—C8 174.8 (6)°]. 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. Since the previously studied mixed azines all had twisted azine bridges, the impervious nature of one phenyl ring with respect to the other is not an entirely surprising result. The azine bridge in mixed azine (1), however, is barely twisted, and the molecule is almost perfectly planar. Therefore, based on the extended π-system and planarity of (1), we would expect a high degree of conjugation from one phenyl ring, through the azine bridge to the other phenyl ring, and a large contribution from resonance forms such as (1a) to the ground state of (1).

(1a)

The importance of resonance form (1a) should be manifest through a structural comparison of mixed azine (1) with the symmetrical azine 4-methoxybenzaldazine, (2), (R = H, X = Y = OMe; Astheimer *et al.*, 1985). If there existed a substantial decrease in the C12—O1, C9—C8 and N2—N1 bond lengths, and a significant increase in the C8=N2 bond length in (1) with respect to (2), then this would suggest that conjugation plays a role in the ground state of (1). Table 1 shows the four pertinent bond lengths for (1) and (2). Although azine (2) is symmetrical, the lattice environment causes it to assume an asymmetric structure in the crystal. Therefore, we draw a comparison between the C12—O1, C8=N2, C9—C8, and N2—N1 bond distances in (1) and the average of these bond distances in (2). The C—O, C—C, and N—N bonds in (1) are all 0.01 Å shorter, and the C=N bond is 0.02 Å longer, than the respective bonds in (2). The direction of the bond length changes are all consistent with a contribution from (1a) to the ground state of (1), however the magnitude of the changes are all quite small and other factors may deem
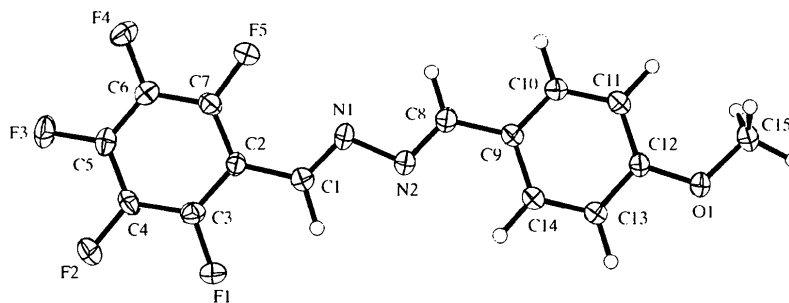
Fig. 1. *ORTEP*II (Johnson, 1976) drawing of mixed azine (1). The displacement ellipsoids are drawn at the 50% probability level.

it unwarranted to attribute them solely to electronic effects. The two C—O bond distances in the symmetric azine (2) differ by as much as 0.01 Å, and this difference is entirely due to crystal lattice effects. Likewise, the small bond-length differences between (1) and (2) could also result from packing.

The crystal packing of mixed azine (1) (Fig. 2) is dominated by face-to-face arene–arene interactions. The crystal lattice contains double face-to-face contacts, *C*, and single face-to-face contacts. The arene–arene interactions in the double face-to-face contacts are always between the methoxy substituted phenyl ring of one mixed azine and the pentafluorinated phenyl ring of another mixed azine. The phenyl–phenyl distances in the double face-to-face contacts are quite small. The shortest distance from a carbon in one phenyl ring to a carbon in the other phenyl ring is 3.31 Å and the average phenyl–phenyl distance is less than 3.65 Å. This is consistent with previously determined phenyl–phenyl distances between a highly fluorinated phenyl ring and a non-fluorinated phenyl ring. The phenyl–phenyl distances in the crystal structures of the hexafluorobenzene/hexadeuterobenzene complex (Williams *et al.*, 1992) and the hexamethylbenzene/hexafluorobenzene complex (Dahl, 1973) are of the same order of magnitude as in (1).

The single face-to-face contacts only occur between two pentafluorinated phenyl rings or two methoxy substituted phenyl rings. The phenyl–phenyl distances between the two pentafluorinated phenyl rings also are very small. The shortest distance between a C atom on one pentafluorinated phenyl ring and another pentafluorinated phenyl ring is 3.33 Å, and the average distance between the two phenyl rings is less than 3.43 Å. The single face-to-face contact between two methoxy-substituted phenyl rings is offset and therefore short phenyl–phenyl distances are found only between three C atoms on each ring, and the shortest distance is 3.45 Å. There is no literature precedence, to the authors knowledge, to which we can compare the short face-to-face distances between the pentafluorinated phenyl rings. The crystal structure of hexafluorobenzene (Bertolucci & Marsh, 1974) does not offer a suitable reference because the dominant intermolecular packing motif is the arene–arene T-contact, and there are no face-
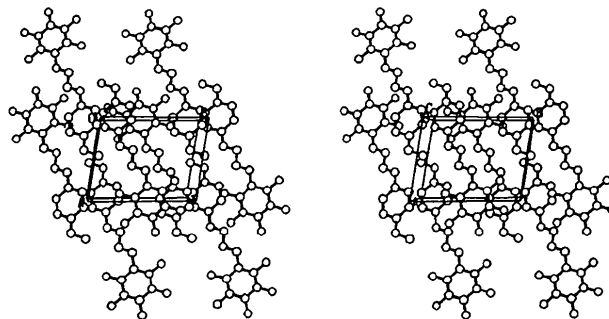

Fig. 2. The crystal packing of mixed azine (1) looking down the *c* axis. The origin is at the upper left, the *a* axis is vertical and the *b* axis horizontal.

to-face arene–arene contacts. The same problem occurs when trying to find a reference to compare the face-to-face contacts between the two methoxy-substituted phenyl rings. The crystal structure of symmetrical azine (2) does not suffice because there are no arene–arene face-to-face contacts in the lattice; there are only arene–arene T-contacts.

The double and single face-to-face arene–arene contact distances are all quite short, and this may be an indication of charge transfer within the lattice. The bright yellow color of (1) further supports this notion. *Ab initio* quantum mechanical calculations are currently being performed to better understand the face-to-face contacts in (1).

Experimental

For the preparation of (1), 4-methoxybenzaldehyde (diethoxyphosphinyl)hydrazone (1.43 g, 0.0050 mol) was dissolved in dry benzene (10 ml) under nitrogen in a three-neck round-bottomed flask. Sodium hydride (50%, 0.30 g, 0.0063 mol) was added to the flask through a funnel, and benzene (5 ml) was used to rinse the funnel. The mixture was stirred for 30 min, then pentafluorobenzaldehyde (1 g, 0.0051 mol) in benzene (10 ml) was added dropwise over 30 min. The reaction mixture became cloudy and was allowed to stir overnight. The benzene solution was decanted from the solid precipitate, washed with three 20 ml portions of water, dried over magnesium sulfate, and rotatory evaporated to yield 0.90 g of a yellow solid. The solid was recrystallized from hexane to yield an off-white solid. Thin-layer chromatography (silica gel, eluting with methylene chloride) showed two spots,

one of which was the hydrazone starting material. Proton NMR also showed the hydrazone. Column chromatography on silica gel, eluting with methylene chloride, yielded 130 mg (7.9% overall yield) of mixed azine (1) as a crystalline yellow solid. The triclinic crystal was obtained by slow diffusion of hexane into a solution of (1) in chloroform.

Crystal data

$C_{15}H_9F_5N_2O$	Mo $K\alpha$ radiation
$M_r = 328.24$	$\lambda = 0.70930$ Å
Triclinic	Cell parameters from 1647
$P\bar{1}$	reflections
$a = 6.8822\,(8)$ Å	$\theta = 5.0{-}25.0°$
$b = 8.9557\,(10)$ Å	$\mu = 0.15$ mm^{-1}
$c = 11.0364\,(12)$ Å	$T = 293$ K
$\alpha = 98.765\,(2)°$	Prism
$\beta = 92.365\,(2)°$	$0.30 \times 0.20 \times 0.15$ mm
$\gamma = 98.660\,(2)°$	Yellow
$V = 663.18\,(13)$ Å^3	
$Z = 2$	
$D_x = 1.644$ Mg m^{-3}	
D_m not measured	

Data collection

Siemens SMART CCD area-detector diffractometer	1776 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.017$
Absorption correction:	$\theta_{max} = 27°$
multi-scan (SADABS;	$h = -8 \rightarrow 8$
Blessing, 1995)	$k = -11 \rightarrow 11$
$T_{min} = 0.954$, $T_{max} = 0.977$	$l = 8 \rightarrow 14$
3918 measured reflections	Intensity decay: <2%
2720 independent reflections	

Refinement

Refinement on F	$w = 1/[\sigma^2(F) + 0.002F^2]$
$R = 0.058$	$(\Delta/\sigma)_{max} = 0.001$
$wR = 0.075$	$\Delta\rho_{max} = 0.28$ e Å^{-3}
$S = 1.19$	$\Delta\rho_{min} = -0.34$ e Å^{-3}
1776 reflections	Extinction correction: none
208 parameters	Scattering factors from International Tables for X-ray Crystallography (Vol. IV)
H-atom parameters constrained	

Table 1. *Selected geometric parameters (Å, °)*

F1—C3	1.344 (3)	O1—C15	1.447 (4)
F2—C4	1.343 (3)	N1—N2	1.407 (3)
F3—C5	1.335 (3)	N1—C1	1.282 (4)
F4—C6	1.346 (3)	N2—C8	1.291 (4)
F5—C7	1.346 (3)	C1—C2	1.463 (4)
O1—C12	1.356 (3)	C2—C3	1.398 (4)
N2—N1—C1	111.5 (3)	N1—C1—C2	121.9 (3)
N1—N2—C8	111.3 (3)	N2—C8—C9	121.5 (3)
C1—N1—N2—C8	174.8 (6)	N2—N1—C1—C2	−180.0 (5)
N1—N2—C8—C9	179.0 (5)	N1—C1—C2—C3	178.4 (6)
N1—C1—C2—C7	0.4 (3)	N2—C8—C9—C10	178.8 (6)
N2—C8—C9—C14	−2.6 (3)		

H atoms were placed in calculated positions with C—H 1.08 Å and U(H) = U(C) + 0.01, and treated as riding during refinement.

Data collection: *SMART* (Siemens, 1995). Cell refinement: *SAINT* (Siemens, 1995). Data reduction: *SAINT*. Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Pro-

gram(s) used to refine structure: *NRCVAX* (Gabe et al., 1989). Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *NRCVAX*.

References

Astheimer, H., Walz, L., Haase, W., Loub, J., Muller, H. J. & Gallardo, M. (1985). *Mol. Cryst. Liq. Cryst.* **131**, 343–351.
Bertolucci, M. D. & Marsh, R. E. (1974). *J. Appl. Cryst.* **7**, 87–88.
Blessing, R. H. (1995). *Acta Cryst.* **A51**, 33–38.
Chen, G. S., Wilbur, J. K., Barnes, C. L. & Glaser, R. (1995). *J. Chem. Soc. Perkin Trans.* 2, pp. 2311–2317.
Dahl, T. (1973). *Acta Chem. Scand.* **27**, 995–1003.
Gabe, E. J., Le Page, Y., Charland, J.-P., Lee, F. L. & White, P. S. (1989). *J. Appl. Cryst.* **22**, 384–387.
Glaser, R. & Chen, G. S. (1998). *J. Comput. Chem.* **19**, 1130–1140.
Glaser, R., Chen, G. S., Anthamatten, M. & Barnes, C. L. (1995). *J. Chem. Soc. Perkin Trans.* 2, pp. 1449–1458.
Glaser, R., Chen, G. S. & Barnes, C. L. (1993). *J. Org. Chem.* **58**, 7446–7455.
Hathaway, B. S., Day, G. M., Lewis, M. & Glaser, R. (1998). *J. Chem. Soc. Perkin Trans.* 2, 2713–2720.
Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Lewis, M., Barnes, C. L. & Glaser, R. (1998). *Can. J. Chem.* **76**, 1371–1378.
Sheldrick, G. M. (1985). *SHELXS86. Program for the Solution of Crystal Structures.* University of Göttingen, Germany.
Siemens (1995). *SMART* and *SAINT. Area-Detector Control and Integration Software.* Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Williams, J. H., Cockcroft, J. K. & Fitch, A. N. (1992). *Angew. Chem. Int. Ed. Engl.* **31**, 1655–1657.

Naphthalene-2,3-dicarbaldehyde

DOYLE BRITTON

Department of Chemistry, University of Minnesota, Minneapolis, MN 55455-0431, USA. E-mail: britton@chemsun.chem.umn.edu

Abstract

The molecular structure of the title compound, $C_{12}H_8O_2$, is normal. The two CHO groups are rotated 7.2 (1) and 22.7 (1)° out of the mean plane of the naphthalene