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Study of Halogen Mediated Weak Interactions in a Series of Halogen Substituted Azobenzenes

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ABSTRACT

The azobenzenes, known for their various importance in the industry, have been chosen as model compounds to understand the role of weak interactions involving C–X (X = F, Cl and Br) bond using single crystal X-ray diffraction technique, especially in the absence of other stronger intermolecular forces such as hydrogen bonds. The fluorinated compounds have been found to pack in the lattice by utilizing C–H···F hydrogen bonds whereas, the chlorinated and brominated analogues have been found to prefer C–X···X–C, C–X···π and π···π interactions while packing in the lattice. The stabilization energy offered by the C–H···F hydrogen bonds and the C–X···X–C interactions have been estimated by computational methods using Gaussian 09 and the topological properties have been determined by using AIM2000 package. The lattice energy decomposition has been done using semi-classical density sums (SCDS) PIXEL method. Our studies indicate that the stabilization energy offered by each C–H···F hydrogen bond lies in the range -0.8 to -1.0 kcal/mol while that for the C–X···X–C interaction has been found to be -0.35 kcal/mol for the X = Cl interaction and -0.73 kcal/mol for the X = Br interaction. Further, the analysis of these interaction by Atoms In Molecules (AIM) theory indicates that the electron densities (ρ_c) at the bond critical points (BCP) for C–H···F and C–X···X–C (X = Cl and Br), calculated using AIM2000 package, are small (<0.007 eÅ^{-3}) and the values of *Laplacian* ($\nabla^2\rho_c$) are positive. This indicates that these interactions are of the hydrogen bond type. A detailed study of these interactions by experimental and computational methods has been described in the manuscript.

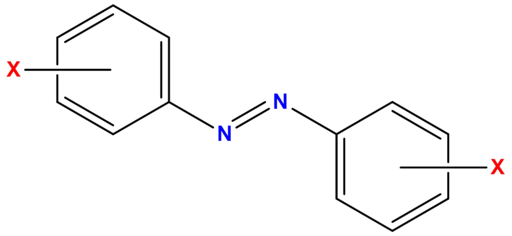
KEYWORDS: azobenzenes, weak interactions, organic fluorine, CLP, topological analysis, AIM.

▪ Introduction and aim of study

We have been interested in the structural study of small organic molecules containing one or more C–X (X = F, Cl and Br) bonds in order to understand the role of the halogens in the crystal packing. This area has become vibrant and controversial in the last decade.[1,2] It has been pointed out by a number of researchers that fluorine behaves differently compared to its congeners in the crystal lattice. The C–F group, termed as "organic fluorine",[2] has been shown to be a poor acceptor of hydrogen bonds[3] and does not offer any stabilizing intermolecular interactions. This inactivity has been attributed to the non-polarizable nature of the fluorine atom.[2a] Recently the review by Berger *et al.*,[4a] the highlight by Chopra and Guru Row[4b] and the perspective by Chopra[4c] have emphasized the role of the C–F bond in crystal engineering. The role of F, Cl and Br in the crystal packing in a series of isoquinoline derivatives have been shown in the literature.[1a,b] The influence of organic fluorine in crystal engineering has been highlighted by Dikundwar *et al.*, in their recent report[5a] on fluorophenylacetylenes and in the cases of fluorobenzenes earlier,[5b] both by *in-situ* crystallization technique.[5b] It is clear from the literature that C–Cl, C–Br and C–I groups offer various intermolecular interactions, which stabilize a number of crystal structures.[6] It is believed that the heavier halogens (Br and I) being more polarizable prefer to form halogen···halogen interactions of various types.[7] Desiraju and Parthasarathy[7a] classified halogen···halogen interactions as type I and type II based on geometrical parameters derived from the Cambridge Structural Database (CSD)[8] analysis. In a recent study, Tothadi, Joseph and Desiraju revisited[9] the halogen···halogen (C–X···X–C) interactions based on the latest version of CSD[10] released in November 2012. They defined the $\angle$C–X···X = θ_1 and the $\angle$X···X–C = θ_2 and proposed that the contacts with $0^\circ \le |\theta_1 - \theta_2| \le 15^\circ$ be termed as type I, those with $15^\circ \le |\theta_1 - \theta_2| \le 30^\circ$ be termed as quasi type I / type II and those with $|\theta_1 - \theta_2| \ge 30^\circ$ be classified as type II halogen···halogen interactions. A number of recent literature has pointed out that organic fluorine is also capable of offering various types of weak interactions such as C–H···F, C–F···π and C–F···F and provides stability to the crystal packing.[11] We have recently reported the structural investigation of a series of fluorine substituted N-benzylideneanilines.[1d] In this article it has been shown that the intermolecular C–H···F hydrogen bonds provide stabilization energy ranging from 1 to 5 kcal/mol. In the present manuscript we would like to bring out the structural variations observed in the cases of F, Cl and Br substituted azobenzenes, which are similar to the previously studied fluorine substituted N-benzylideneanilines in terms of the molecular motif.

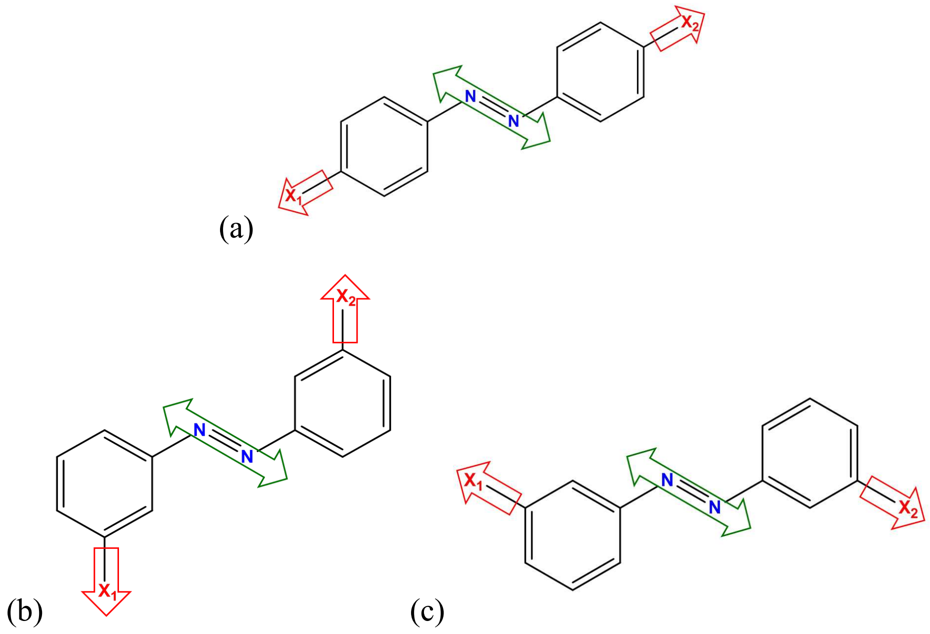
Azobenzene (Ph-N=N-Ph) and substituted azobenzenes are widely used as dyes[12] due to their brilliant colors. The color originates from the -N=N- chromophoric unit. Further, the color variations in these compounds are due to different substitutions over aromatic rings, which are attached to the chromophroic unit. These substitutions on the aromatic ring can alter the extent of π-electron conjugation over the molecule; which in turn has resulted into the different colors among the halogen substituted azobenzenes. Such substituted azobenzene systems have been found to have potential applications as photoswitches[13] and modifying agents for peptides, oligonucleotides and transmembrane proteins.[14] The direct conversion of light into mechanical energy by the help of substituted azobenzenes has been well documented.[15] The opto-mechanical properties and their *E-Z* isomerization studies highlight the importance of these molecules for their future applications. The substitution of halogen (X) atom(s) at *para*-, *meta*-, and *ortho*- positions of the phenyl ring of the azobenzenes has been found to generate a series of highly interesting molecules having a range of different colors (characterized by different absorption maxima and the corresponding molar extinction coefficients) and anomalous melting pattern. Hence, a systematic study of the crystal structures of halogen (X = F, Cl and Br) substituted azobenzene is conducted. Our aim in this manuscript is to compare the role of F, Cl and Br in crystal packing and to determine the strength and nature of these interactions provided by C–X (X = F, Cl and Br) group using both experimental and computational methods. Cambridge Structural Database (CSD) search on the halogen substituted azobenzenes indicated the unavailability of the structures of most of the compounds and hence we have synthesized and spectroscopically characterized all of them in order to structurally demonstrate the role of the halogen substitution in azobenzene. The compounds have been crystallized from various solvents and the crystal structures have been determined using the single crystal X-ray diffraction data sets collected at 100 K. The intermolecular interactions have been studied using standard methods described in the experimental section. The strength of the intermolecular interactions observed in these molecular crystals have been quantitatively estimated by *ab-initio* methods using Gaussian 09[16] and the topological properties of these intermolecular interactions in the terms of electron density (ρ_c) bond critical points (BCP) have been analyzed using AIM2000 package.[17] The semi-classical density sums (SCDS) PIXEL[18] method has been used for the decomposition of the lattice energy into columbic (E_{COUL}), polarization (E_{POL}), dispersion (E_{DISP}) and repulsion (E_{REP}) components in order to understand the nature of the intermolecular forces responsible for the formation of the lattice.

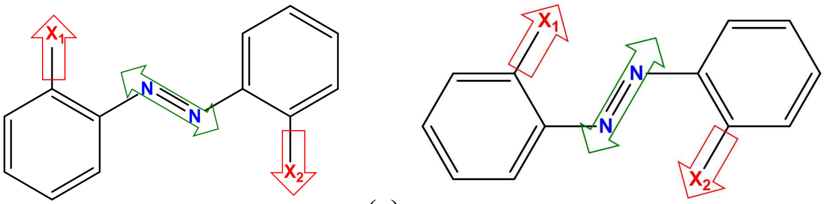
The scheme 1 displays the list and numbering scheme of the compounds studied and the scheme 2 displays the various possible conformations of the *E* isomers of halogen substituted (symmetrical) azobenzenes. The *ortho*- and *meta*- substituted *E*-azobenzenes are capable of having two conformers as shown in the scheme 2. These conformers have been found to have energies in the range from 0.5 to 22.6 kcal/mol (Table S2, ESI). It would be interesting to see which conformation is governing the crystal packing in the solid state and what kind of structural features offered by these molecules.



X = 4F (AZ01), 3F (AZ02), 2F (AZ03)
X = 4Cl (AZ04), 3Cl (AZ05), 2Cl (AZ06)
X = 4Br (AZ07), 3Br (AZ08), 2Br (AZ09)

Scheme 1: Chemical scheme of all the compounds studied.





(d) (e)

Scheme 2: (a) The only conformation of *para*- substituted *E*-azobenzene, (b) Conformation A of the *meta*- substituted *E*-azobenzene, (c) Conformation B of the *meta*- substituted *E*-azobenzene, (d) Conformation A of the *ortho*- substituted *E*-azobenzene, (e) Conformation B of the *ortho*- substituted *E*-azobenzene.

▪ Experimental section

Starting materials

All the halogen substituted anilines were purchased from Sigma Aldrich, India and were used without further purification. Solvents and reagents were purchased from Merck Chemicals, India and used as received.

Synthesis and Characterization

Compounds AZ01 to AZ09 (Scheme 1) were synthesized from their corresponding anilines following the procedure reported in the literature.[19] CuBr (0.03 mmol), pyridine (0.09 mmol), and halogenated aniline (1 mmol) were mixed in toluene (4 mL) under air (1 atm). The reaction mixture was stirred vigorously (1500 rpm) at 60 ^{o}C for 20 h. The reaction mixture was then cooled to room temperature and toluene was removed under vacuum. The crude product was purified by flash chromatography on a short silica gel (230-400 mesh size) column using hexane as eluent. All the compounds were characterized by ^{1}H, ^{13}C NMR (400MHz, Bruker Biospin Avance-III NMR spectrometer) (Figure S1-18, ESI), FTIR (Bruker Tensor 72, equipped with diamond cell ATR) (Figure S19-27, ESI), and the melting points were determined by Differential Scanning Calorimetry (DSC) (Figure S28-36, ESI). Powder X-ray diffraction data (PXRD) were recorded on a Rigaku Ultimia IV diffractometer using parallel beam geometry, Cu – Kα radiation, 2.5° primary and secondary solar slits, 0.5° divergence slit with 10 mm height limit slit, sample rotation stage (120 rpm) attachment and DTex Ultra detector. The tube voltage and current applied were 40 kV and 40 mA respectively. The data sets were collected over 2θ ranging from 5 to 50° with a scanning speed of 5° per minute with 0.02° step (Figure S37-45, ESI). All the purified compounds were found to have characteristic color (Figure S46, ESI). UV-Vis (UV 3000+, Lab India) spectroscopic experiments were carried out to identify the characteristic $\pi\rightarrow\pi^*$ and $n\rightarrow\pi^*$ transitions and the molar extinction coefficients at the λ_{max} (Table S1, ESI) for all the compounds reported in this manuscript. Good quality single crystals were grown from dichloromethane/hexane or methanol/ethyl acetate solvents by slow solvent evaporation technique at 4 ^{o}C and Single crystal X-ray diffraction data for all the compounds were collected using Bruker AXS KAPPA APEX-II CCD diffractometer (Monochromatic Mo – Kα radiation) equipped with Oxford cryosystem 700Plus at 100 K. Data collection and unit cell refinement for the data sets were done using Bruker APEX-II suit,[20] data reduction and integration were performed by SAINT V7.685A[20] (Bruker AXS, 2009) and absorption corrections and scaling was done using SADABS V2008/1[20] (Bruker AXS). The crystal structures were solved by using Olex2[21] or WinGx[22] packages using SHELXS97[23] and the structures were refined using SHELXL97.[23] Single crystal data and the results of the structure refinement are listed in the Table 1. All the Figures including the packing and interaction diagrams have been generated using Mercury.[24] Geometric calculations including the least square plane angle calculations have been done using PARST[25] and PLATON.[26] The intermolecular interactions observed in these compounds are listed in the Table 2. The PXRD patterns were simulated using Mercury from the CIFs generated by Olex2. These simulated patterns were compared with the experimental PXRD patterns (recorded on bulk samples) of the respective azobenzenes.

Interaction energy and topological parameters calculations:

a) Interaction energy calculations by Gaussian:

The interaction energy calculations were performed by using Gaussian 09[16] at the Møller–Plesset perturbation theory (MP2) level using 6–31+G(d,p) basis set. Gauss View[27] has been used as a graphical interface for Gaussian 09. The primary coordinates for the molecules under study were taken from their respective experimentally determined crystal structures (from CIFs, data was recorded at 100 K). The energy of the monomers ($E_{monomer}$) and the dimers (E_{dimer}) were calculated using the same method and were corrected for basis set superposition error (BSSE) using counterpoise method. The interaction energies (ΔE_{dimer}) of the dimeric motifs were calculated using the formula $\Delta E_{dimer} = E_{dimer} - (2 \times E_{monomer})$. When both C–H···π and C–H···F interactions were found to be present in given dimer, to estimate the interaction energy offered by only C–H···F interaction, we replaced the interacting F atom by H atom (at a distance of 0.95 Å from the C atom) and carried out the gas phase stabilization energy calculations ($\Delta E_{CH\pi}$). This stabilization energy is due to the C–H···π interaction present between these two molecules. Therefore the contribution of C–H···F hydrogen bond in the stabilization energy of the dimer (ΔE_{total}) can be calculated as $\Delta E_{total} - \Delta E_{CH\pi}$. The interaction energies calculated for the interactions involving the halogens are listed in the table 2. The single point energies of the two possible conformers (Scheme 2) have been calculated at the same level of theory and method.

b) Topological parameters calculations by AIM2000 package:

The suitable wave function files were generated by using Gaussian 09 for the dimers and those wave function files were used as inputs for AIM2000 package[13] for the analysis of topological parameters like electron densities (ρ_c) and Laplacian ($\nabla^2\rho_c$) at the bond critical points (BCP). The intermolecular interactions were analyzed on the basis of above calculated parameters and while calculating these properties all the default options were used in the package.

c) Coulomb-London-Pauli (CLP) energy calculations:

Intermolecular interaction energies were calculated using the semi-classical density sums (SCDS) PIXEL method, which was implemented within the 2011 version of the CLP model of intermolecular interaction package. The calculated interaction energies are partitioned into columbic (E_{COUL}), polarization (E_{POL}), dispersion (E_{DISP}) and repulsion (E_{REP}) components, and they are expected to be accurate within a range of 1–2 KJ/mol. The initial NAME.CIFs were generated by using Olex2 package and edited manually to convert into CSD CIF format. NAME.oih files were generated by using *retcif* module available within the CLP package. NAME.oeh and NAME.dat files were generated subsequently by using *rector* interface module of CLP package. The required input files for PIXELC were generated by using *pixmt2* server module which reads NAME.oeh and generates NAME.gif and NAME.inp files. NAME.den files (files that contain the molecular electron density generated at MP2 level and 6-31G** basis set) were then generated by running Gaussian09 using NAME.gif file as input. NAME.inp and NAME.den files along with the parameter controller file PIXPAR.par were used to calculate Lattice energy of a cluster of molecules with maximum distance from the central molecule of 40Å and a top radius for search of 50Å. After successful completion of the calculation the output file contains partitioned total energies in the form of E_{COUL}, E_{POL}, E_{DISP} and E_{REP}. The package generates two output files namely NAME.pri (a printout file with the results of the calculation) and NAME.mlc (a file with molecule-molecule energies). The partitioned lattice energies for the molecules studied are listed in the Table 3.

▪ Results

The compounds AZ01 to AZ08 were found to crystallize in the monoclinic $P2_1/c$ space group while AZ09 was found to crystallize in the monoclinic $C2/c$ space group. All the molecules possessing inversion center (C_i) were found to crystallize with Z' = 0.5 and the crystallographic center of inversion being coincident with the molecular center of inversion laying at the midpoint of the –N=N– bond.

Packing features of compounds 1-9:

1. (E)-bis(4-fluorophenyl)diazene (AZ01):

The molecules were found to pack in the lattice by weak bifurcated (at both donor and acceptor sites) C–H···F hydrogen bonded network as shown in the Figure 1. A very weak π···π interaction has been noticed in this structure along the *a*-axis with the inter-planar distance of 3.4 Å with the distance between the centroids of the interacting rings being 3.8 Å (same as the cell length along *a*-axis). No C–H···π interaction was observed in this structure. The gas phase stabilization energy of the dimer formed by the C2–H2···F1 (-x, y - ½, ½ - z) (H2···F1 = 2.63(1) Å, ∠C2-H2···F1 = 141(1)^o) has been found to be -0.96 kcal/mol while that of the dimer formed by other C2–H2···F1 (1-x, y - ½, ½ - z) (H2···F1 = 2.68(1) Å, ∠C2–H2···F1 = 127(1)^o) hydrogen bond has been found to be -0.83 kcal/mol. Further, the analysis of these interactions by using AIM shown that, the existence of bond critical points for both the C2–H2···F1 hydrogen bonds. The ρ_c at these BCPs are 0.004 and 0.005 eÅ^{-3} respectively, and the values of $\nabla^2(\rho_c)$ at these BCPs have been found to be 0.023 and 0.026 eÅ^{-5} respectively.

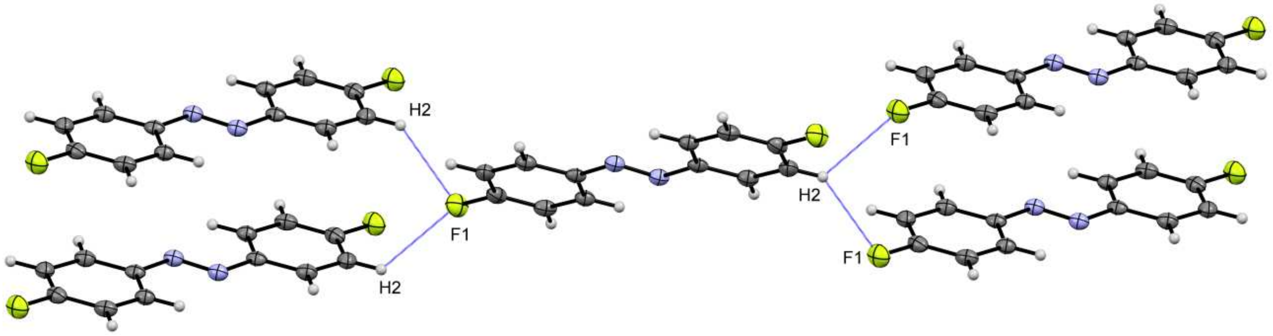


Figure 1: The bifurcated C–H···F bonds in AZ01.

2. (E)-bis(3-fluorophenyl)diazene (AZ02):

The molecules have been found to form centrosymmetric dimers involving C6–H6···F1 hydrogen bonds and these dimers were fund to be connected to another dimer by the same C–H···F hydrogen bonds. Further, these chains of dimers were found to be connected by another C4–H4···F1 hydrogen bond (Figure 2). The H5 and H1 hydrogen atoms were also involved in the C–H···π interactions as shown in the Figure 2. The gas phase stabilization energy of the dimer formed by the C6–H6···F1 (1-x, -y, -1-z) (H6···F1 = 2.55(1) Å, ∠C6–H6···F1 = 136(2)^{o}) hydrogen bond has been found to be -1.82 kcal/mol. It is noteworthy that the stabilization energy for this dimer is nearly double than that in the cases of the C–H···F hydrogen bonded dimer found in AZ01. This stabilization energy in case of AZ02 may be attributed to two C–H···F hydrogen bonds present between the two molecules, which formed the dimer. The stabilization energy of the dimer formed by C4–H4···F1 (x, -y-½, z-½) (H4···F1 = 2.56(1) Å, ∠C4–H4···F1 = 155(2)^{o}) hydrogen bond and C–H···π interactions has been found to be -4.53 kcal/mol. The stabilization energy only due to the C–H···π interaction is -3.62 kcal/mol. The contribution of C4–H4···F1 hydrogen bond in the stabilization is -0.92 kcal/mol, similar to those found in the dimers of AZ01 and AZ02. The BCPs for these interactions were located from AIM calculations and the ρ_c at these BCPs are 0.006, 0.006 and 0.005 eÅ^{-3} respectively, and the values of $\nabla^2(\rho_c)$ at these BCPs have been found to be 0.030, 0.030 and 0.028 eÅ^{-5} respectively. The stabilization energy due to the formation of C5–H5···Cg1(π) has been found to be -2.80 kcal/mol. The conformer 2b has been found to be more stable by 2.45 kcal/mol than the conformer 2c. Hence, we have not observed the appearance of this conformer B (Scheme 2c) in the crystal structure.

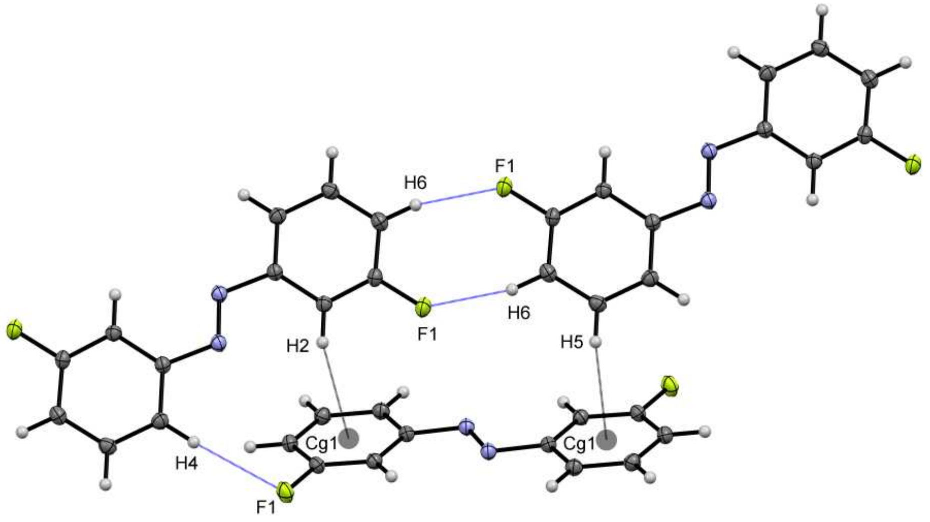


Figure 2: Interconnected chains of dimers by C–H···F hydrogen bonds and C–H···π interactions in AZ02.

Table 1: The crystallographic and refinement data for the compounds AZ01 to AZ09.

Identification code	**AZ01**	**AZ02**	**AZ03**	**AZ04**	**AZ05**	**AZ06**	**AZ07**	**AZ08**	**AZ09**
CCDC number	883112	883113	883114	883109	883110	883111	883106	883107	883108
Empirical formula	$C_{12}H_8F_2N_2$	$C_{12}H_8F_2N_2$	$C_{12}H_8F_2N_2$	$C_{12}H_8Cl_2N_2$	$C_{12}H_8Cl_2N_2$	$C_{12}H_8Cl_2N_2$	$C_{12}H_8Br_2N_2$	$C_{12}H_8Br_2N_2$	$C_{12}H_8Br_2N_2$
Formula weight	218.20	218.20	218.20	251.10	251.10	251.10	340.02	340.02	340.02
Crystal size (mm)	0.3×0.2×0.1	0.2×0.2×0.2	0.3× 0.1× 0.1	0.4×0.2×0.1	0.2×0.2×0.1	0.2×0.2×0.15	0.2×0.2×0.1	0.2× 0.2× 0.1	0.3×0.1×0.1
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P\,2_1/c$	$P\,2_1/c$	$P\,2_1/c$	$P\,2_1/c$	$P\,2_1/c$	$P\,2_1/c$	$P\,2_1/c$	$P\,2_1/c$	$C2/c$
a (Å)	3.8035(4)	7.1516(6)	9.7795(22)	9.7663(10)	12.7716(2)	11.4948(10)	10.0896(19)	10.9225(8)	21.7149(10)
b (Å)	5.8716(5)	5.8580(5)	3.7350(7)	4.6720(5)	3.8032(4)	3.8134(3)	4.7532(10)	4.4318(3)	3.9697(2)
c (Å)	22.1229(20)	12.2714(10)	13.1877(27)	11.4452(13)	11.6316(11)	13.5210(11)	11.622(2)	11.9113(9)	13.7591(7)
α (^{o})	90.0	90.0	90.0	90.0	90.0	90.00	90.0	90.0	90.0
β (^{o})	91.260(7)	108.672(5)	95.492(9)	91.138(7)	105.903(2)	113.889(2)	91.951(4)	98.145(3)	105.101(3)
γ (^{o})	90.0	90.0	90.0	90.0	90.0	90.00	90.0	90.0	90.0
V (Å^3)	493.94(1)	487.04(7)	479.49(17)	522.12(1)	543.36(9)	541.91(8)	557.02(19)	570.77(3)	1145.10(10)
Z	2	2	2	2	2	2	2	2	4
Z'	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
ρ_{calc} (g cm^{-3})	1.467	1.488	1.511	1.597	1.535	1.539	2.027	1.978	1.972
Temperature (K)	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
μ/ mm^{-1}	0.115	0.117	0.119	0.589	0.566	0.568	7.246	7.072	7.050
$\theta_{min,\ max}$	3.59- 28.68	3.01-30.49	3.1-26.37	2.09-28.28	3.32-25.03	3.07-33.42	2.02-25.03	3.69-25.02	3.07-25.03
F(000)	224.0	224.0	224.0	256.0	256.0	256.0	328.0	328.0	656.0
$h_{min,\ max}$; $k_{min,\ max}$; $l_{min,\ max}$;	-3 5 -7 7 -29 29	-10 10 -8 6 -14 17	-12 6 -4 3 -16 16	-12 13 -6 6 -15 15	-11 15 -4 3 -13 9	-17 17 -5 4 -18 20	-12 11 -4 5 -13 13	-13 13 -5 4 -14 14	-25 25 -4 4 -16 15
No. of reflections collected	3385	3656	2286	4584	2185	4709	2632	2748	3865
R_{int}	0.0433	0.0215	0.0251	0.0201	0.0150	0.0124	0.0209	0.0184	0.0204
No. of unique reflections	1259	1480	982	1295	958	1959	975	1006	1016
No. of parameters / restraints	73 / 0	73 / 0	73 / 0	73 / 0	73 / 0	73 / 0	73 / 0	79 / 18	73 / 0
R_1 [I > 2σ(I)]	0.0567	0.0400	0.0386	0.0269	0.0273	0.0272	0.0214	0.0235	0.0218
wR_2 (all data)	0.1605	0.1164	0.0943	0.0685	0.0704	0.0768	0.0575	0.0585	0.0613
GooF	1.060	1.037	1.048	1.075	1.069	1.073	1.093	1.033	1.061
Largest diff. Peak/Hole/e Å^{-3}	0.352/-0.203	0.457/-0.230	0.180/-0.196	0.417/-0.250	0.264/-0.169	0.618/-0.335	0.556/-0.637	0.484/-0.290	0.670/-0.432

Table 2: The list of intermolecular interactions and stabilization energy values (kcal/mol) for AZ01 to AZ09 compounds.

Compound code	**D–B···A**	**D···A/Å**	**B···A/Å**	**∠(D–B···A)/º**	**Symmetry**	**Stabilization Energy (kcal/mol)**
AZ01	C2–H2···F1	3.419(2)	2.629(1)	141(1)	- x, y - ½, ½ - z	-0.96
	C2–H2···F1	3.338(2)	2.679(1)	127(1)	1 - x, y - ½, ½ -z	-0.83
AZ02	C6–H6···F1	3.299(1)	2.550(1)	136(2)	1 - x, - y , - z - 1	-1.82[*]
	C4–H4···F1	3.454(1)	2.569(1)	155(2)	x, - y - ½, z - ½	-0.91[**]
	C2–H2···Cg1	3.487(1)	2.831(2)	125(1)	- x, ½ + y, ½ - z	-3.61[**]
	C5–H5···Cg1	3.448 (1)	2.751(1)	129(1)	1-x, y - ½, ½ - z	-2.80
AZ03	C6–H6···F1	3.634(2)	2.727(1)	160(1)	- x, 1 - y, 1 – z	-2.05[**]
	C1–H1···F1	3.212(2)	2.658(1)	117(2)	x, 3/2 - y, z + ½	-1.00[**]
	C3–H3···Cg1	4.447	3.586	152	x, 3/2 -y, z + ½	-3.23[**]
AZ04	C2– H2···Cl1	3.904(1)	2.990(1)	162(1)	1 - x, 2 - y, 1 – z	-1.00
	C1–Cl1···Cl1	-	3.418(6)	167(1)	1 - x, y - ½, ½ -z	-0.35
	C1–Cl1 ···Cg1	3.871(2)	3.447(8)	90 (1)	x, 1 + y, z	-9.99
AZ05	C4–H4···Cl1	3.820(2)	2.976(1)	149(1)	1 - x, 1 - y, 1 – z	-1.54
	Cg1···Cg1	3.803	-	-	x, y-1, z	-9.67
	C1–Cl1···Cl1	-	3.519(2)	124(1)	1 - x, ½ +y, ½ - z	-0.28
AZ06	Cg1···Cg1	3.813	-	-	x, y - 1, z	-10.36
	C2–H2···Cl1	3.656(1)	2.997(1)	128 (1)	x, 3/2 - y, z - ½	-4.15[#]
	C1–H1···Cl1	3.448	2.990	111(1)		
AZ07	C1–Br1···Br1	-	3.526(8)	167(1)	1-x, y - ½, ½ - z	-0.73
	C1–Br1···Cg1	3.952(3)	3.526(1)	88(1)	x, y - 1,z	-11.17
AZ08	Cg1···Cg1	4.432	-	-	x, y - 1, z	-12.25
	C1–Br1···Br1	-	3.669	155(1)	2 - x, y – ½, 3/2 - z	-0.57
AZ09	Cg1···Cg1	3.970	-	-	x, y - 1, z	-11.14
	C1–H1···Br1	3.763	3.116	126(1)	x, 2-y, ½ + z	-4.37
	C1–H1···Br1	3.775	3.148	125(1)		
	C1–H2···Br1	3.600	3.137	112(1)		

[*] There are two C6–H6···F1 interactions between the two molecules.

[**] The procedure used for calculation of these values is described in the text.

[#] There are two C–H···Cl interactions between the two molecules.

Table 3: Contributions of coulombic, polarization, dispersion and repulsion components for lattice energies for compounds AZ01 to AZ09 (kcal/mol).

Code	E_{COUL}	% E_{COUL}	E_{POL}	% E_{POL}	E_{DISP}	% E_{DISP}	E_{REP}	% E_{REP}	Total
AZ01	-7.6	12.7	-3.01	5.0	-30.8	51.4	18.57	30.9	-22.9
AZ02	-8.7	13.7	-3.13	5.0	-31.7	50.2	19.67	31.1	-23.9
AZ03	-8.3	13.0	-3.39	5.3	-32.5	50.8	19.69	30.8	-24.5
AZ04	-12.6	13.0	-5.26	5.4	-47.2	48.8	31.64	32.7	-33.4
AZ05	-11.1	12.9	-5.66	6.6	-42.4	49.5	26.6	31.0	-32.6
AZ06	-11.3	13.3	-5.11	6.0	-42.4	50.0	26.05	30.7	-32.8
AZ07	-12.9	14.0	-4.64	5.0	-43.3	47.1	31.05	33.8	-29.8
AZ08	-10.0	12.3	-4.3	5.3	-41.0	50.6	25.74	31.8	-29.5
AZ09	-11.0	13.9	-4.33	5.4	-39.3	49.4	24.86	31.3	-29.8

3. (E)-bis(2-fluorophenyl)diazene (AZ03):

The molecules were found to form chains of dimers by C6–H6···F1 hydrogen bonds in two different directions. These two sheets of the chains of dimers are further connected to each other by C1–H1···F1 hydrogen bonds (Figure 3). The gas phase stabilization energy of the dimer formed by C6–H6···F1 hydrogen bonds (-x, 1-y, 1-z) (H6···F1 = 2.73(1) Å, ∠C6–H6···F1 = 160(1)^{o}) has been found to be -2.05 kcal/mol. This dimer also has two identical C–H···F hydrogen bonds between the two interacting molecules. The stabilization energy for the other dimer formed by C1–H1···F1 (x, 3/2 - y, ½ + z) (H1···F1 = 2.66(1) Å, ∠C1–H1···F1 = 117(2)^{o}) hydrogen bond and the C3–H3···Cg1(π) interaction has been found to be -4.23 kcal/mol. The stabilization energy due to the C3–H3···Cg1(π) interaction has been found to be -3.23 kcal/mol and that due to C–H···F hydrogen bond is calculated to be -1.00 kcal/mol. The ρ_c at the BCPs of C6–H6···F1 and C1–H1···F1 are 0.004, 0.003 and 0.005 eÅ^{-3} respectively and the values of $\nabla^2(\rho_c)$ at these BCPs have been found to be 0.020, 0.020 and 0.026 eÅ^{-5} respectively. The conformer 2d has been found to be more stable by 9.12 kcal/mol than the conformer 2e. Hence, we have not observed the appearance of this conformer B (Scheme 2e) in the crystal structure.

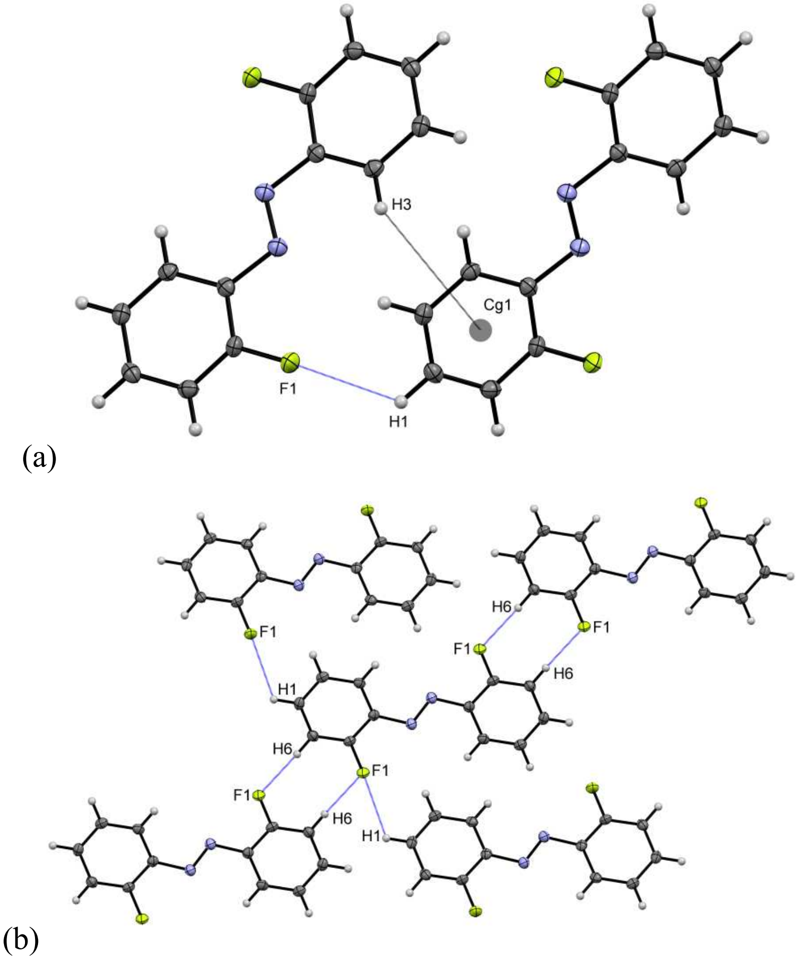


Figure 3: (a) Dimers of AZ03 formed by C–H···F and C–H···π interactions, (b) Chain of dimers formed by C–H···F interactions.

4. (E)-bis(4-chlorophenyl)diazene (AZ04):

The structure of this compound was reported in 1969 by Hope and Victor.[28] We re-determined the structure for studying the intermolecular interactions and for computational purpose. The molecules have been found to pack by type II C–Cl···Cl–C halogen contacts and C–Cl···π interactions (Figure 4a). The gas phase stabilization energy of the dimer formed by C–Cl···Cl interaction (1-x, y- ½, ½ -z) (Cl1···Cl1 = 3.418(6) Å, ∠C1–Cl1···Cl1 = 167(1)^{o}) has been found to be -0.35 kcal/mol, which is less than those observed earlier in the cases of C–H···F hydrogen bonded dimers. The ρ_c at the BCP of the Cl···Cl contact was calculated by AIM and it was found to be 0.007 eÅ^{-3} and the value of $\nabla^2(\rho_c)$ at this CP has been found to be 0.030 eÅ^{-5}. Further, molecular chains of dimers have been found to form by very weak C2–H2···Cl1interactions as shown in the Figure 4b. The stabilization energy due to the formation of this dimer was found to be -1.00 kcal/mol. The ρ_c and the $\nabla^2(\rho_c)$ at this critical point have been found to be 0.004 eÅ^{-3} and 0.018 eÅ^{-5} respectively.

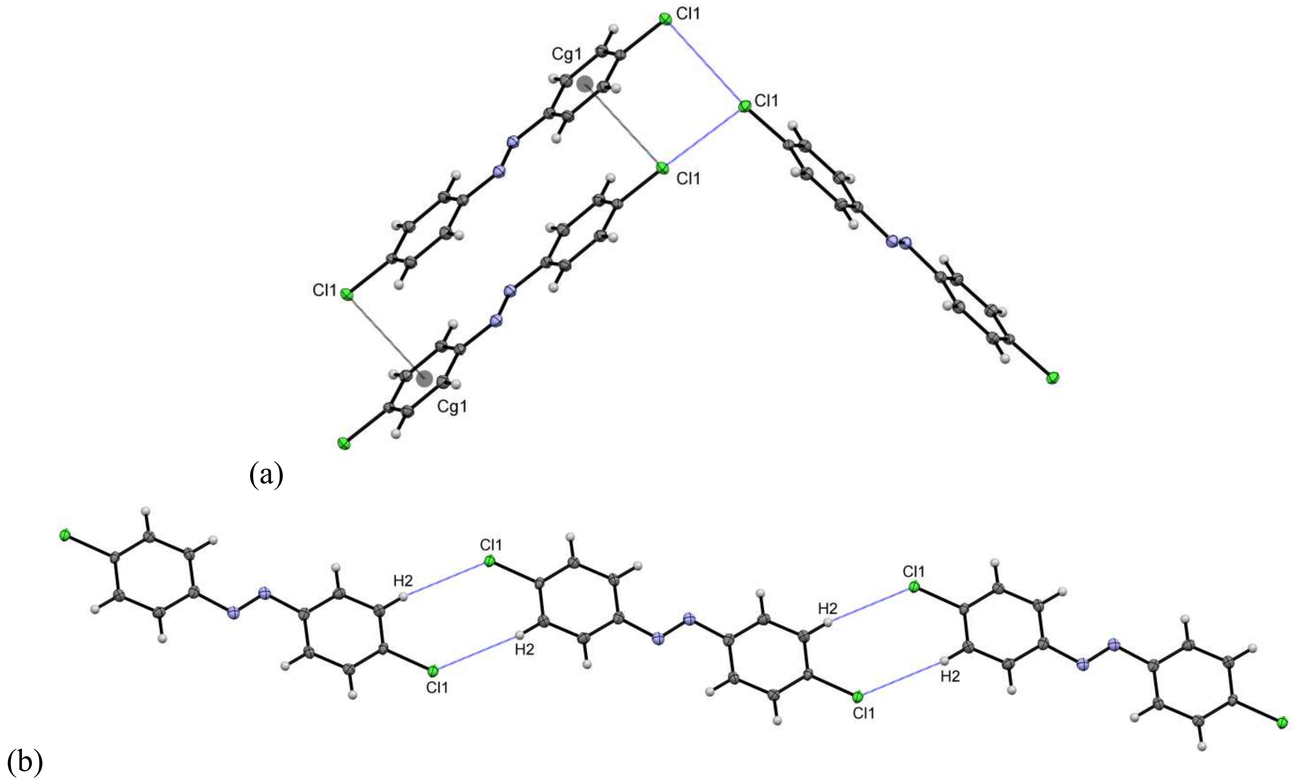


Figure 4: (a) The C–Cl···Cl–C contacts and C–Cl···π interactions in AZ04. Dummy atoms are placed at the midpoints of the delocalization for pictorial representation, (b) Chains of dimers by C–H···Cl interactions.

5. (E)-bis(3-chlorophenyl)diazene (AZ05):

The molecules are found to be packed in the crystal lattice by involving weak C–H···Cl interactions (Figure 5a), slipped π stacking interactions and C–Cl···Cl interactions (Figure 5b). The stabilization energy for the dimer formed by two C4–H4···Cl1 interactions have been found to be -1.54 kcal/mol and that of the dimer formed by the π stacking has been found to be -9.67 kcal/mol. The same for the dimer formed by C1–Cl1···Cl1 interaction has been found to be -0.28 kcal/mol. The ρ_c at the BCPs of the C4–H4···Cl1 and C1–Cl1···Cl1 have been found to be 0.005 and 0.005 eÅ^{-3} respectively and the values of the corresponding $\nabla^2(\rho_c)$ have been found to be 0.020 and 0.023 eÅ^{-5} respectively.

The conformer 2b has been found to be more stable by 0.73 kcal/mol than the conformer 2c. Hence, we have not observed the appearance of this conformer B (Scheme 2c) in the crystal structure.

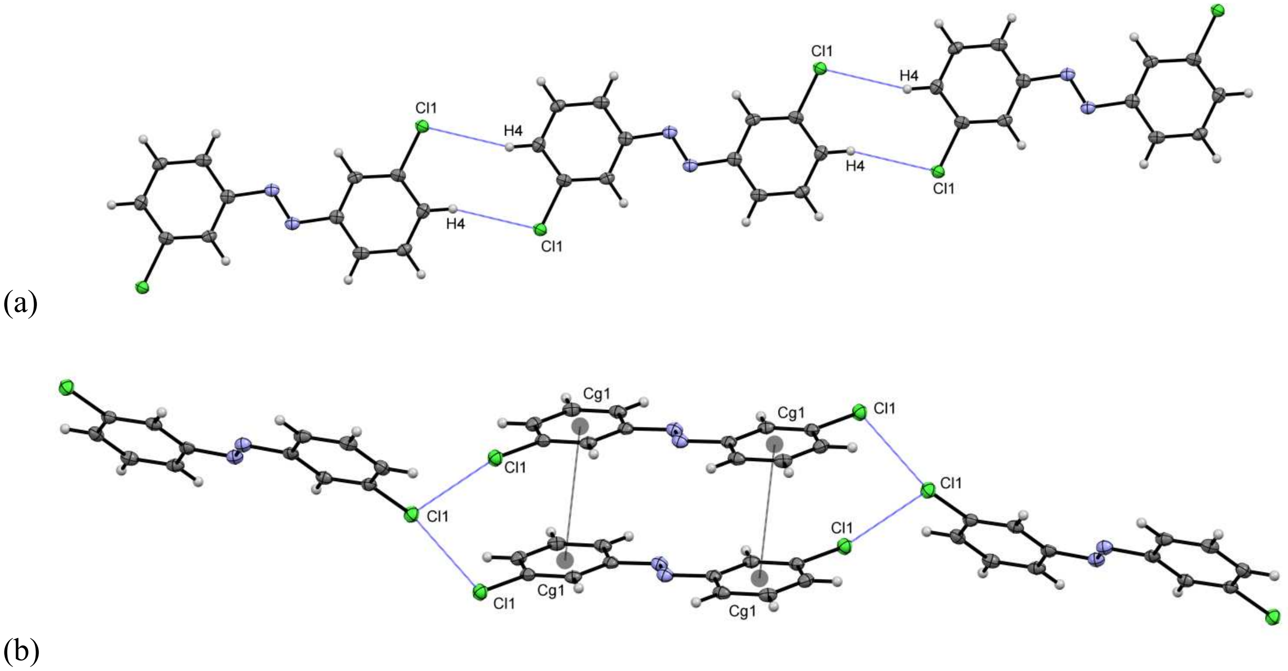


Figure 5: (a) Chains of dimers by C–H···Cl interactions, (b) π stacking and C–Cl···Cl interactions in AZ05.

6. (E)-bis(2-chlorophenyl)diazene (AZ06):

A room temperature structure for this compound was reported in the literature.[29] We have re-determined the structure at 100 K to compare it with other structures and for our computational purpose. The conformer 2d has been found to be more stable by 22.59 kcal/mol than the conformer 2e. Hence, we have not observed the appearance of this conformer B (Scheme 2e) in the crystal structure. The molecules were found to pack by very weak π stacking interactions between two adjacent molecules in fully eclipsed condition and no other interactions were observed (Figure 6). The centroid (Cg) to centroid (Cg) distance was found to be 3.970Å. The stabilization energy due to the dimer formation by two C–H···Cl interactions have been found to be -4.15 kcal/mol. The ρ_c at the critical points are found to be 0.005 and 0.005 eÅ^{-3} for C1–H1···Cl1 and C2–H2···Cl1 respectively. The $\nabla^2(\rho_c)$ for these are found to be 0.022 and 0.022 eÅ^{-5} respectively.

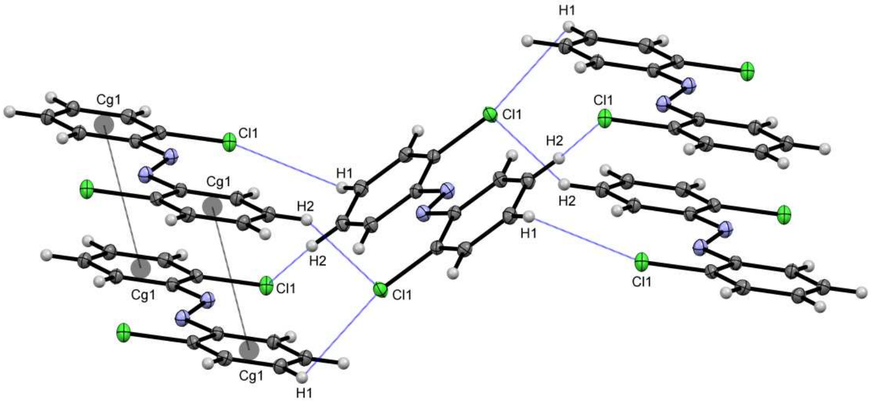


Figure 6: Formation of linkage between two π stacked columns by C–H···Cl interactions.

7. (E)-bis(4-bromophenyl)diazene (AZ07):

This compound has been found to have two polymorphs, both crystallizing in $P2_1/c$ with different unit cell parameters as reported in the literature.[30,31] The polymorph reported by Amit and Hope in 1966 (CSD refcode AZBNBT) doesn't have hydrogen atoms in the CIF and we were unable to re-grow this polymorph. We observed that the polymorph reported by Amit and Hope does not have any C–Br···Br interaction or π stacking interaction. The second polymorph was reported by Howard *et al.,* in 1994 (CSD refcode AZBNBT01). We have re-determined the structure of this second polymorph for our calculation purposes. This was found to be iso-structural (Unit cell similarity Index 1.02) with the corresponding chloro analog (AZ04). The molecules were found to pack in the crystal lattice by a type II C–Br···Br–C contacts, C–Br···π interactions and a π stacking between the aromatic ring (Figure 7) as observed in the case of chloro analog AZ04. The gas phase stabilization energy of the dimer formed by C1–Br1···Br1 interaction (1-x, y- ½, ½ -z) (Br1···Br1 = 3.526(8) Å, ∠C1–Br1···Br1 = 167(1)^{o}) has been found to be -0.73 kcal/mol. The ρ_c at BCP of the C–Br···Br interaction was calculated by AIM and it was found to be 0.008 eÅ^{-3} and the value of $\nabla^2(\rho_c)$ at this BCP has been found to be 0.028 eÅ^{-5}.

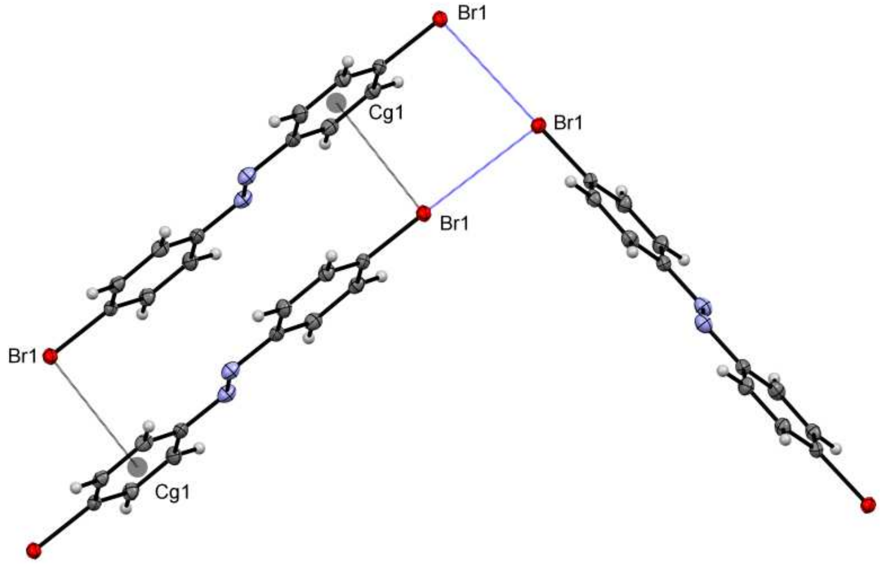


Figure 7: C–Br···Br–C interactions and C–Br···π interactions in AZ07.

8. (E)-bis(3-bromophenyl)diazene (AZ08):

The asymmetric unit was found to contain half of the molecule in two locations with the occupancy ratio of 0.70:0.30. On growing these fragments across the center of inversion located at the center of the –N=N– bond, we observed that the two fragments have resulted into two different conformers (as shown in the Scheme 2c and 2d) of the *E*-isomer. It was found to have similar unit cell parameters as compared to AZ05 (Unit cell similarity Index 0.97) but AZ05 did not show the existence of the molecule in two different conformers. The existence of the two conformers in the crystal lattice of AZ08 has resulted into a disorder, which has been referred to as molecular motion like the motion of a pair of paddles by Harada *et al.*[32] The conformer 2b has been found to be more stable by 0.52 kcal/mol than the conformer 2c. This difference being the lowest, probably it was possible for this molecule to adopt the high energy conformation for some of the molecules at the crystallization condition and hence we observed the appearance of the high energy conformer in the crystal structure of this compound reported here. The similar trend was reported by Harada *et al.,* in 1997 in the cases of (*E*)2,2′-dimethylazobenene, (*E*)3,3′-dimethylazobenene, and (*E*)4,4′-dimethylazobenene.[32] The molecules of AZ08 have been found to pack in the crystal lattice involving weak C–Br···Br–C (type II), π···π stacking and C–H···π interactions between the –N=N– and the centroid of the aromatic ring (Figure 8). The stabilization energy due to the C–Br···Br–C contact have been found to be -0.57 kcal/mol and the ρ_c and the $\nabla^2(\rho_c)$ at the critical point have been found to be 0.007 eÅ^{-3} and 0.021 eÅ^{-5} respectively. It is noteworthy that in case of AZ05, π···π stacking and C–H···Cl interactions were observed while in AZ08, C–Br···Br–C, π···π stacking and C–H···π interactions have been observed. Hence, though the unit cell similarity index of it with AZ05 is close to 1, they are not isostructural.

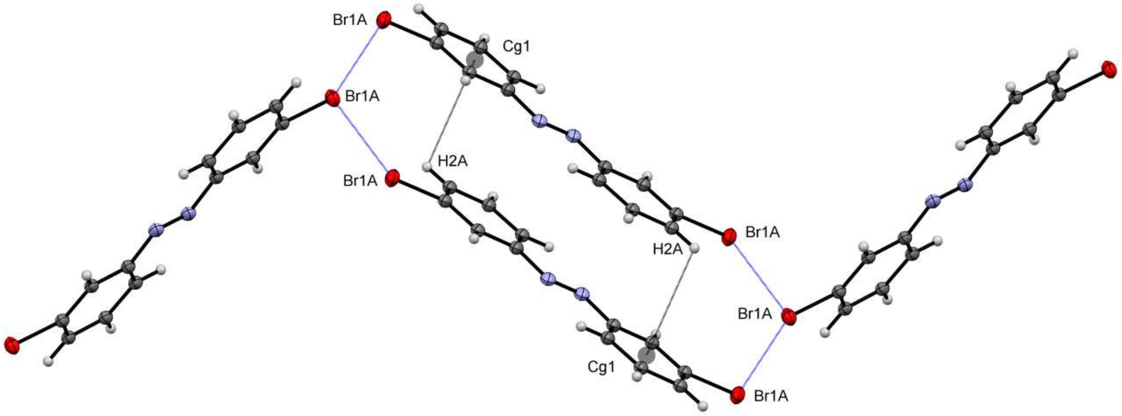


Figure 8: C–H···π and C–Br···Br interactions in AZ08.

9. (E)-bis(2-bromophenyl)diazene (AZ09):

It is interesting to note that the unit cell parameters and the space group of AZ06 are not similar to those of AZ09, but both AZ06 and AZ09 are found to pack by identical packing features. AZ09 also pack by very weak π stacking (Figure 9) as observed in AZ06 (Figure 6b). The stabilization energies for these interacting dimers are listed in the table 2.

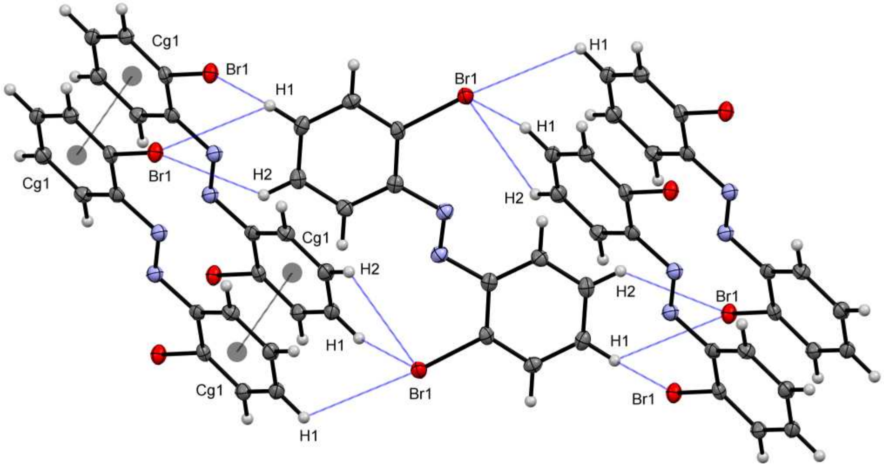


Figure 9: Molecular assembly in AZ09 formed by π stacking and weak C–H···Br interactions.

▪ Discussion

The detailed structural and intermolecular interaction energy study of the halogen substituted azobenzenes indicates that, these compounds majorly oriented in stable *trans* (*E*) conformation. The fluorinated *E*-azobenzenes (AZ01-AZ03) have preferred to be packed by the formation of chains and dimers by utilizing C–H···F hydrogen bonds whereas, the Cl and Br substituted molecules (AZ04-AZ09) have prefers to be packed by halogen···halogen interactions and π stacking. The fluorinated *E*-azobenzenes were found to form chains or dimers by utilizing C–H···F hydrogen bonds. These stabilization energies have been calculated at their respective isolated crystal geometries as have been done by Panini and Chopra recently.[33] Unlike their calculations, we did not move the H atoms to their respective neutron distances, rather we kept the crystal geometry unchanged for the gas phase calculations. The stabilization energy for a pair of molecules forming a chain (by one C–H···F hydrogen bond) or a dimer (by two C–H···F hydrogen bonds) have been found to be closed to -0.9 and -1.8 kcal/mol respectively. The stabilization energies offered by intermolecular C–H···π interactions in AZ02 and AZ03 have been found to be -3.61 and -3.23 kcal/mol. Although the stabilization energy offered by the C–H···π interaction (>3 kcal/mol/interaction) is more as compared to the stabilization energy provided by each C–H···F hydrogen bond (<1 kcal/mol), yet the compounds AZ01-03 have been found to crystallize in different lattices and to pack in different ways. The unsubstituted azobenzene was found to pack in a different unit cell at room temperature (296 K) and was found to have two crystallographically independent molecules (disordered) in the asymmetric unit with C_i symmetry in both the molecules.[31] It was further observed that the disorder, which was observed in the data collected at 296 K, was not present in the low temperature data (82 K). This feature has not been observed in any of these nine compounds. Therefore it may be inferred that although the stabilization energy offered by the C–H···F hydrogen bond is <1 kcal/mol/interaction, they are capable of playing an observable role in guiding the crystal packing in these fluorinated azobenzenes; otherwise all the three fluorinated azobenzenes (AZ01-03) would have been found to crystallize in the same unit cell with the same space group and would have shown similar packing features as shown by their unsubstituted analogue. This inference is further supported by the fact that AZ02 and AZ03 have been found to form the chains of dimers, rather than forming ribbons (Figure 2a and 3a), by the involvement of two identical C–H···F hydrogen bonds between a pair of molecules across the inversion centre while the molecules of AZ01 have preferred to pack *via* bifurcated C–H···F hydrogen bonds (Figure 1) and C–H···π interaction has not been encountered in this case. The compounds AZ04 to AZ08 have been found to pack by type II halogen···halogen contacts whereas, the compound AZ09 has been found to pack by C–H···Br interactions and very weak π stacking between phenyl rings. Out of these nine molecules only AZ08 showed paddle motion[32] while AZ02 and AZ03 displayed C–H···π interactions and AZ04 and AZ07 shown C–X···π (X = Cl and Br) interactions also. Further, the analysis of these intermolecular interactions by the AIM theory indicates that these interactions are of the hydrogen bond type. The ρ_c and the $\nabla^2(\rho_c)$ at the bond critical point between the interacting atoms are in the range of 0.004 – 0.008 eÅ^{-3} and 0.020 – 0.030 eÅ^{-5} respectively. The molecules reported in this manuscript have been found to have the conformations displayed in the Scheme 2(b) and 2(d) for the fluoro and chloro compounds whereas, for the bromo compound, the conformation 2(c) has also been observed. It is evident from SCDS-PIXEL method calculations (Table 3), that the contribution of the dispersion forces (nearly 50%) is the maximum for all the compounds studied. In fact, all the various other components for all the compounds show similar trend. This indicates that these molecules prefer to pack majorly by dispersion interactions and not by coulombic or polarization forces.

▪ Conclusion

We would like to infer that the intermolecular interactions mediated by “organic fluorine” cannot be neglected. The replacement of F by H has resulted into a significant change in the electronic environment of the molecule and which has been reflected in the altered packing of the molecules in comparison to its non-fluorinated analogue has been. Further, the replacement of F by Cl and Br has also resulted into different packing features as shown in this manuscript. We have considered a few more weak intermolecular interactions, which are at distances marginally longer (0.05 to 0.15Å) than the sum of the van der Waals radii of the interacting atoms, involving Cl and Br and have calculated the stabilization energies and topological properties for those interactions as well. The influence of C–F group in the stereoelectronic factors of a molecule and its surroundings needs further discussion. Whether these interactions are at all important for the packing or not can only be ascertained by a thorough experimental charge density analysis, which is beyond the scope of this publication. This is being carried out currently by us and will be highlighted in a future publication. To understand the role of weak interactions offered by C–X (X = F, Cl and Br) bond in more detail, we are in the process of analysing the structures of unsymmetrically substituted azobenzenes and tetra fluoroazobenzens. Further the possibility of the dimerization of these azobenzenes by [2+2] cycloaddition is also being explored.

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Supporting Information Available: All the crystal structures are deposited with CCDC and the depository numbers are 883106 - 883114. The CIFs are also provided as supporting information along with ^{1}H and ^{13}C NMR spectra, FTIR spectra, UV-VIS data, PXRD traces, DSC traces and ORTEP diagrams. This information is available free of charge via the Internet at http://pubs.acs.org/.

References

(1) (a) Choudhury, A. R.; Urs, U. K.; Guru Row, T. N.; Nagarajan. K. *J. Mol. Struct*. **2002**, *605*, 71–77, (b) Choudhury, A. R.; Guru Row, T. N. *Cryst. Growth Des.* **2004**, *4*, 47–52, (c) Choudhury, A. R.; Nagarajan, K.; Guru Row, T. N. *Cryst. Engg.* **2004**, *6*, 43-55, (d) Choudhury, A. R.; Guru Row, T. N.

CrystEngComm **2006,** *8,* 265–274, (e) Kaur, G.; Panini, P.; Chopra, D.; Choudhury, A. R. *Cryst. Growth Des*. **2012**, *12*, 5096−5110.

(2) (a) Dunitz, J. D.; Taylor, R. *Chem. Eur. J.* **1997**, *3*, 89−98, (b) Dunitz, J. D. *ChemBioChem*. **2004**, *5*, 614−621.

(3) (a) Howard, J. A. K.; Hoy, V. J.; O'Hagan, D.; Smith, G. T. *Tetrahedron*. **2006**, *52*, 12613−12622, (b) O'Hagan, D. *Chem. Soc. Rev*. **2008**, *37*, 308−319.

(4) (a) Berger, R.; Resnati, G.; Metrangolo, P.; Weber, E.; Hulliger, J. *Chem. Soc. Rev*. **2011**, *40*, 3496−3508 and references therein, (b) Chopra, D.; Guru Row, T. N. *CrystEngComm* **2011**, *13*, 2175−2186 and references therein, (c) Chopra, D. *Cryst. Growth Des*. **2012**, *12*, 541−546.

(5) (a) Dikundwar, A. G.; Sathishkumar, R.; Guru Row, T. N.; Desiraju, G. R. *Cryst. Growth Des*. **2011**, *11*, 3954–3963, (b) Thalladi, V. R.; Weiss, H. C.; Bla¨ ser, D.; Boese, R.; Nangia, A.; Desiraju, G. R. *J. Am. Chem. Soc.* **1998**, *120*, 8702−8710.

(6) (a) Prasanna, M. D.; Guru Row. T. N. *CrystEngCommun*. **2000**, *2*, 134-140, (b) Chopra, D.; Nagarajan, K.; Guru Row, T. N. *J. Mol. Struct*. **2008**, *888*, 70−83.

(7) (a) Desiraju, G. R.; Parthasarathy, R. *J. Am. Chem. Soc.* **1989**, *111*, 8725-8726, (b) Pedireddi, V. R.; Reddy, D. S.; Goud, B. S.; Craig, D. S.; Aare, A.; Desiraju, G. R. *Perkin Trans. 2.* **1994**, 2353-2360.

(8) Allen, F. H.; Bellard, S.; Brice, M. D.; Cartwright, G. A.; Doubleday, A.; Higgs, H.; Hummelink, T.; Hummelink-Peters, B. J.; Kennard, O.; Motherwell, W. D. S.; Rodgers, J. R.; Watson, D. G. *Acta Crystallogr*. **1979**, *835*, 2331-2339.

(9) Tothadi, S.; Joseph, S.; Desiraju, G. R. *Cryst. Growth Des.* **2013**, *13*, 3242-3254.

(10) The Cambridge Structural Database version 5.34. ConQuest 1.15; Cambridge Crystallographic Data Centre: Cambridge, U.K., Nov 2012, Feb 2013 update.

(11) (a) Chopra, D.; Guru Row, T. N. *Cryst. Growth Des*. **2005**, *5*, 1679−1681, (b) Chopra, D.; Guru Row, T. N. *CrystEngComm* **2008**, *10*, 54−67, (c) Chopra, D.; Guru Row, T. N. *Cryst. Growth Des*. **2008**, *8*, 848−853, (d) Nayak, S. K.; Reddy, M. K.; Guru Row, T. N.; Chopra, D. *Cryst. Growth Des*. **2011**, *11*, 1578−1596, (e) Panini, P.; Chopra, D. *CrystEngComm* **2012**, *14*, 1972−1989.

(12) (a) Hunger, K. Industrial Dyes: Chemistry, properties, Applications; Wiley-VCH, Weinheim, 2003, (b) Anderson, R. G.; Nickless, G. *Analyst,* **1967**, *92*, 207–238, (c) Cation, S. C.; Farris, E. Concise encyclopedia of Chemical Technology, Wiley, 1985.

(13) (a) Bléger, D.; Schwarz, J.; Brouwer, A. M.; Hecht. S. *J. Am. Chem. Soc*. **2012**, *134*, 20597−20600, (b) Wegner. H. A. *Angew. Chem. Int. Ed*. **2012**, *51*, 4787–4788, (b) Beharry, A. A.; Woolley, G. A. *Chem. Soc. Rev*. **2011**, *40*, 4422−4437, (c) Brieke, C.; Rohrbach, F.; Gottschalk, A.; Mayer, G.; Heckel, A. *Angew. Chem., Int. Ed*. **2012**, *51*, 8446−8476.

(14) (a) Fehrentz, T.; Scho□nberger, M.; Trauner, D. *Angew. Chem., Int. Ed*. **2011**, *50*, 12156−12182, (b) Polosukhina, A.; Litt, J.; Tochitsky, I.; Nemargut, J.; Sychev, Y.; De Kouchkovsky, I.; Huang, T.; Borges, K.; Trauner, D.; Van Gelder, R. N; Kramer, R. H. *Neuron*. **2012**, *75*, 271−282.

(15) (a) Bléger, D.; Yu, Z. L.; Hecht, S. *Chem. Commun*. **2011**, *47*, 12260−12266, (b) Finkelmann, H.; Nishikawa, E.; Pereira, G. G.; Warner, M. *Phys. Rev. Lett*. **2001**, *87*, 015501, (c) Hugel, T.; Holland, N. B.; Cattani, A.; Moroder, L.; Seitz, M.; Gaub, H. E. *Science* **2002**, *296*, 1103−1106.

(16) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.;

Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian 09, Revision A.1; Gaussian, Inc.: Wallingford, CT, 2009.

(17) (a) Bader, R. F. Atoms in Molecules. A Quantum Theory; Clarendon Press: Oxford, U.K., 1990, (b) König, F. B.; Schönbohm, J.; Bayles, D. *J. Comp. Chem*. **2001**, *22*, 545-559, (c) König, F.B.; Schönbohm, J.; Bayles, D. *J. Comp. Chem*. **2002**, *23*, 1489-1494.

(18) Gavezzotti, A. *New J. Chem*. **2011**, *35*, 1360-1368.

(19) Chun, Z.; Ning, J. *Angew. Chem. Int. Ed*. **2010**, *49*, 6174-6177.

(20) APEX2, SADABS and SAINT; Bruker AXS Inc.: Madison, Wisconsin, USA, 2008.

(21) Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *J. Appl. Cryst.* **2009**, *42*, 339-341.

(22) Farrugia, L. J. WinGx, *J. Appl. Cryst.* **1999**, *32*, 837-838.

(23) Sheldrick, G. M. *Acta Crystallogr. A.* **2008**, *64*, 112-122.

(24) Macrae, C. F.; Bruno, I. J.; Chisholm, J. A.; Edgington, P. R.; McCabe, P.; Pidcock, E.; Rodriguez-Monge, L.; Taylor, R.; van de Streek, J.; Wood, P. A. *J. Appl. Crystallogr.* **2008**, *41,* 466-470.

(25) Nardelli, M. *J. Appl. Cryst*. **1995**, *28*, 569.

(26) Spek, A. L. *Acta Crystallogr*. **2009**, D65, 148−155.

(27) GaussView, Version 5, Dennington, R.; Keith, T.; Millam, J. Semichem Inc., Shawnee Mission KS, 2009.

(28) Hope, H.; Victor, D. *Acta. Crystallogr*. **1969**, *B25*, 1849−1853.

(29) Komeyama, M.; Yamamoto, S.; Nishimura, N.; Hasegawa, S. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 2606−2607.

(30) Amit, A. G.; Hoppe, H. *Acta. Chim. Scand.* **1966**, *20,* 835−844.

(31) Howard, J. A. K.; Batsanov, A.; Bryce, M. R.; Chesney. A. *Acta. Crystallogr*. **1994**, *C50*, 1818−1819.

(32) Harada, J.; Ogawa, K.; Tomoda, S. *Acta Crystallogr.* **1997**, *B53*, 662−672.

(33) Panini, P.; Chopra, D. *CrystEngComm*. **2013**, *15*, 3711−3733.

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Study of Halogen Mediated Weak Interactions in a Series of Halogen Substituted Azobenzenes

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The crystal structures of halogen substituted azobensenes have been investigated using single crystal X-ray diffraction technique. The stabilization energies offered by various intermolecular interactions involving the halogen atoms have been calculated using Gaussian09 and the topological properties have been determined using AIM2000. This study indicates that F prefers hydrogen bonding while Cl and Br prefer halogen bonding in crystal structures.