Spectroscopic and theoretical studies on symmetric aryl azines

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Azines, which closely resemble azobenzenes, have important applications in the field of nonlinear optics. NMR and IR spectroscopic study of some symmetric aryl azines has been undertaken with the aid of *ab initio* theoretical calculations. All data indicated that the structure of azine and substituted azines is the symmetric *trans* form.

Keywords: azines, vibrational spectra, *ab initio* calculations

Azines are important in C–C bond formation and react as the ene component in [3 + 2] additions.[1] Azines with donor and acceptor groups [D–C_6H_4–(R)C=N–N=C(R)–C_6H_4–A] at the ends of a π-conjugated backbone behave as a novel non-linear optical materials.[2] Hagen *et al.*[3] from the electron diffraction analysis of the molecular structure of 2,3-diazabuta-1,3-diene (CH_2 = N-N=CH_2) have shown that this compound exists as an equilibrium mixture of *anti* and *gauche* conformers whereas the corresponding tetrabromo derivative exists exclusively in the *gauche* conformer. There are reports of solid state structures of several azines by X-ray diffraction studies[4-6] and configurational and conformational aspects of heterocyclic azines by NMR techniques.[7-9] Analysis of vibrational spectroscopic signals along with NMR data will give detailed information about the structures exhibited by azines. In continuation of our earlier work[10,11] on the ^1H and ^{13}C NMR studies of azines, we now report on the spectroscopic studies of symmetrical azines derived from substituted aryl aldehydes.

Experimental

Materials and methods

The azines were prepared according to the standard procedure reported in the literature.[12] About 0.02 mol of the aryl aldehyde was refluxed with 0.01 mol of hydrazine hydrate in 20 ml ethanol for 3 h and the reaction mixture was poured into crushed ice; the precipitate obtained was crystallised from an ethanol–chloroform (1 : 10) mixture. Yields were in the range 70–85%. IR spectra were recorded on a Nicolet Avatar 360 FT-IR spectrometer. The sample was mixed with KBr and the pellet technique was adopted to record the spectra. Proton spectra were recorded on a Bruker WH 400 NMR spectrometer at 400 MHz. Samples were prepared by dissolving about 10 mg of material in 0.5 ml of $CDCl_3$ containing 1% TMS. The experimental parameters were the following: data points 32 K, number of transients 10; spectral width 4000 Hz. Proton-decoupled ^{13}C spectra were recorded on Bruker WH 400 NMR spectrometer operating at 100 MHz using 10 mm sample tubes. Solutions for the measurement of spectra were prepared by dissolving 0.5 g of the sample in 2.5 ml $CDCl_3$ containing few drops of TMS as internal reference. The solvent $CDCl_3$ also provided the internal field frequency lock signal. The experimental parameters were the following: number of scans 5000; number of data points 32 K, spectral sweep width 22000 Hz, and pulse width 6 μs.

Theoretical calculations

The theoretical calculations presented here were performed with the Gaussian-94/DFT [13]program on an IBM-RS6000 computer system. The molecular geometry of the parent azine was optimised using the HF method with the basis set 6-31G*. A complete geometry optimisation was carried out employing Berny's optimisation algorithm, which resulted in C_S symmetry. The vibrational frequencies and corresponding normal modes were then evaluated at the optimised geometry using analytical differentiation algorithms contained within the program. The assignment of the calculated normal modes was made from the corresponding potential energy distributions (PEDs) and isotopic shifts. The PEDs and frequencies of the isotopically labelled species were calculated from the quantum mechanically derived Cartesian force constant matrix using the MOLVIB program.[14] The normal modes were analysed by transforming the calculated displacements from Cartesian to internal coordinate basis using a program, NMODES.[15] The assignments of the calculated frequencies were clarified by visual inspection of the normal modes using the program MOLVIB. The vibrational frequencies obtained are reported without scaling.

Results

IR, ^1H and ^{13}C NMR spectra were recorded for the azine whose structure is **1a**. The signals in ^1H and ^{13}C spectra were assigned on their positions, integrals, multiplicities and on comparison with those of the corresponding parent aldehyde. There are two possible conformations of C=N groups, namely the s-*trans* and s-*cis* conformations, **2a** and **2b**. Several studies have revealed[16-18] that the s-*cis* (**2a**) form is destabilised due to strong interactions of the *vicinal* electron lone pairs on the nitrogen atoms along with electrostatic effects and steric repulsion of the two ends of groups attached to the *sp* hybridised carbon atoms. Single crystal measurements reported by Mom and Dewith[6] have also revealed that the *N*(1),*N*(2)-*bis*(benzylidene) azine exists in the s-*trans* conformation only.

In the present study the s-*cis* conformation is also ruled out. In the s-*trans* conformation (**2a**) there are two possible configurations of the aryl ring as shown in **3**. In the isomer **3a** both the azomethine protons are *syn* to the N–N bond whereas in isomer **3b** one hydrogen is *syn* to the N–N bond and the other hydrogen is *anti* to the N–N bond. In the isomer **3b**, two different chemical shifts are expected for azomethine protons whereas in the isomer **3a** one signal is expected for a CH=N proton. The observation of only one signal in the ^1H NMR spectra of the azine confirms that the azine exist in the isomeric form '**a**' only. This form is further supported by the following observations. Generally in azines protons which are *syn* to a N–N bond are expected to resonate upfield compared to *anti* protons. Arnal *et al.*[8] have reported that acetal azine [CH_3CH=N–N=CH–CH_3] exists in only one isomeric form in which both the azomethine protons are *syn* to the N–N bond. The azomethine protons resonate upfield (7.89 ppm) relative to the aldehydic proton in acetaldehyde (9.80 ppm). It is seen from Table 1 that azomethine protons resonate considerably upfield in all azines relative to their corresponding aldehydes. The magnitude of shielding ranges from –1.11 to –1.44 ppm. This observation also supports the symmetrical azine existing in the conformer **3a** in which both the azomethine protons are *syn* to the N–N bond.

Study of vibrational frequencies will illuminate the individual vibrational modes which will help in the establishment of the structure exhibited by azines and so *ab initio* vibrational analysis has been carried out on the parent azine **1a**. The azine has 28 atoms having 78 vibrations. The optimised structure of **1a** is shown as **4**. The theoretical IR intensity and Raman activity are plotted against the calculated vibrational frequencies in Fig. 1.

The experimental IR spectra exhibited strong absorptions around 2920 ($\nu_{C\text{-}H}$), 1620 ($\nu_{C=N}$) and 1210 ($\nu_{C=N\text{-}N}$)cm^{-1}. From the visual assignments from the Molvib programme it is inferred that the higher frequency range vibrations (above 3000 cm^{-1}) are due to ring CH symmetric stretching while the frequencies in the range below 1700 cm^{-1} are due to mixed modes. The 1649 and 1659 cm^{-1} absorptions of the calculated frequencies are assigned to the symmetric C=N stretch and asymmetric C=N vibration. As these frequencies are mutually present in both the IR and Raman spectra we can confirm that the azine is in the C_{2h} symmetry. The theoretical vibrational frequencies 327, 550, 1230, 1530 cm^{-1} were mainly due to the N–N atom pair. It is expected[19] that the symmetric N–N stretching vibration will be at 1200–1000 cm^{-1} as a strong Raman line and the absence of this line in the experimental IR spectra further confirms the above conclusion.

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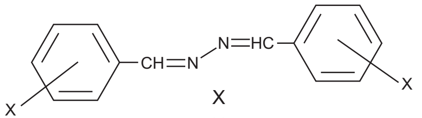
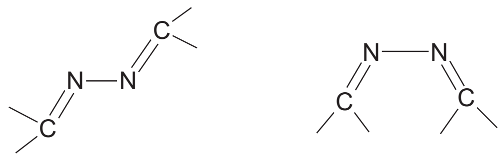


a; H
b; *p*-Cl
c; *o*-Cl
d; *o*-OH

1

Molecular structure of arylazines parent (**a**), *p*-chloro substituted (**b**), *o*-chloro substituted (**c**) and *o*-hydroxy substituted (**d**).

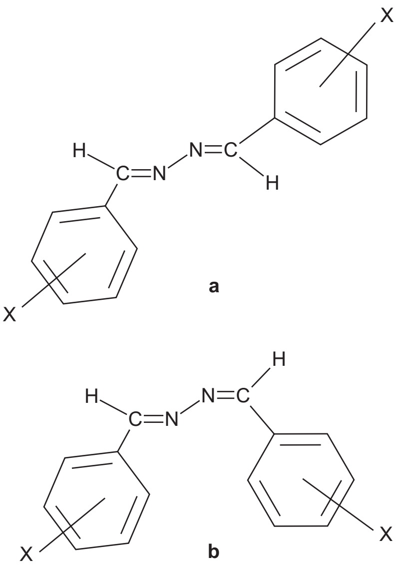


s-*trans* **a**

s-*cis* **b**

2

Isomers of arylazine *trans* configuration (**a**) and *cis* configuration (**b**).

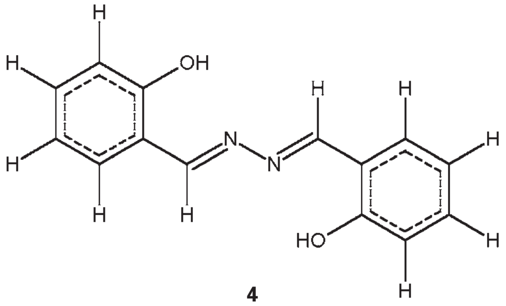


3

Two possible structures of *trans* azine.

Table 1 ^{1}H, ^{13}C NMR chemical shifts (PPM) for the symmetric azines for CH=N

Compound	^{1}H NMR data	^{13}C NMR data
1a	8.73	161.4
2a	9.09	159.1
1c	8.50	153.7
1d	8.71	164.7



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Optimised structure of azine.

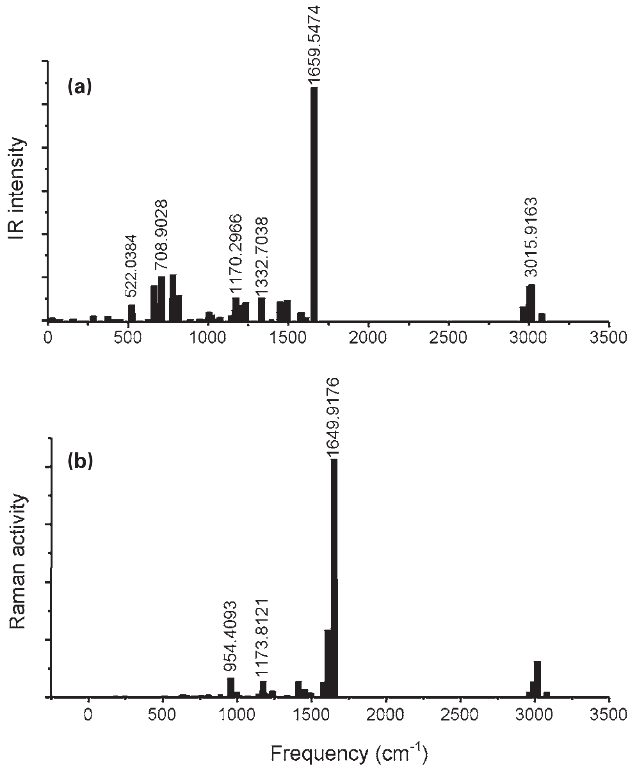

Fig. 1. Theoretical vibrational plots IR (**a**) and Raman activity (**b**).

Substituted symmetric azines

The introduction of substituent in the aryl rings can alter the results. So a series of substituted symmetrical azines (**1b**, **1c**, **1d**) were prepared and the resulting NMR frequencies are also given in the Table 1. It is inferred from the Table 1 that the introduction of a substituent in the *para* position slightly shields the azomethine proton. However, in the case of *N*(1),*N*(2)-bis(*o*-chlorobenzylidene)azine (**1b**) considerable deshielding [+ 0.36 ppm] and shielding [–2.3 ppm] has been observed on the azomethine proton and the corresponding carbons due to the introduction of the chloro substituent in the *ortho* position. This may be due to the steric interaction between the azomethine proton and the bulky chloro substituent which prefers to adopt the *syn* orientation with respect to the azomethine proton. In the preferred orientation, steric polarisation interaction exists between the bulky chloro substituent and the azomethine proton. As a result of this interaction the azomethine protons are deshielded and the corresponding carbons are shielded. In *N*(1),*N*(2)-bis (*o*-hydroxybenzylidene)azine (**1d**)) there is no appreciable change in the chemical shift of the azomethine proton due to the introduction of a hydroxy group in the *ortho* position. The hydroxy group may be oriented towards the azomethine nitrogen since this orientation is stabilised by intramolecular hydrogen bonding between the hydroxy group and azomethine nitrogen. However, considerable deshielding has been observed on the azomethine carbons due to the introduction of the hydroxy group in the *ortho* position. The intramolecular hydrogen bonding increases the electronegativity of the azomethine nitrogen which, in turn, has a deshielding influence on the nearby azomethine carbon.

The IR and Raman frequencies for 2,6-dichlorobenzaldehyde azines are reported in the literature.[20] The symmetric C=N stretching vibration occurs at 1587 cm^{-1} and is explained by the steric hindrance of the two chlorine atoms which prevent the 2,6-dichlorophenyl from being planar with the C=N group. Theoretical and experimental research is in progress on the vibrational spectra of this compound.

Conclusion

From the NMR and vibrational spectroscopic studies all the aryl azines are confirmed as having the symmetric transoid configuration. The theoretical vibrational frequencies along with the experimental observations further support the assignment. The introduction of substituents symmetrically does not alter the configaration.

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