

Computational studies of the structure of aldazines and ketazines.

Part 1. Simple compounds

Ibon Alkorta,^{*} Fernando Blanco,[‡] and José Elguero

Instituto de Química Médica, CSIC, Juan de la Cierva, 3, E-28006 Madrid, Spain

[‡]On leave from the University of Valencia (Faculty of Pharmacy)

E-mail: ibon@iqm.csic.es

Dedicated to Prof. Guy Queguiner on the occasion of his 70th anniversary

Abstract

The molecular structure of seven simple aliphatic and aromatic aldazines and ketazines has been calculated at the B3LYP/6-311++G** computational level. Geometries, *E/Z*- isomerism and conformation of the compounds have been compared with the available data (electron diffraction, X-ray crystallography). IR and Raman spectra have been calculated and compared with experimental ones.

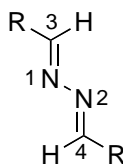
Keywords: Aldazines, ketazines, isomerism, B3LYP, 6-311++G**, IR C=N stretching

Introduction

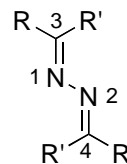
The term azine has two meanings in chemistry: in heterocyclic chemistry, azines are aromatic six-membered rings containing from one (pyridine **I**) to six N atoms (hexazine). In alicyclic chemistry, azines are the compounds resulting from the reaction of two molecules of a carbonyl compound (or, less frequently, of two different carbonyl compounds) with hydrazine. The compounds are called aldazines **II** or ketazines **III** depending on whether the carbonyl compound is an aldehyde or a ketone, respectively.



I

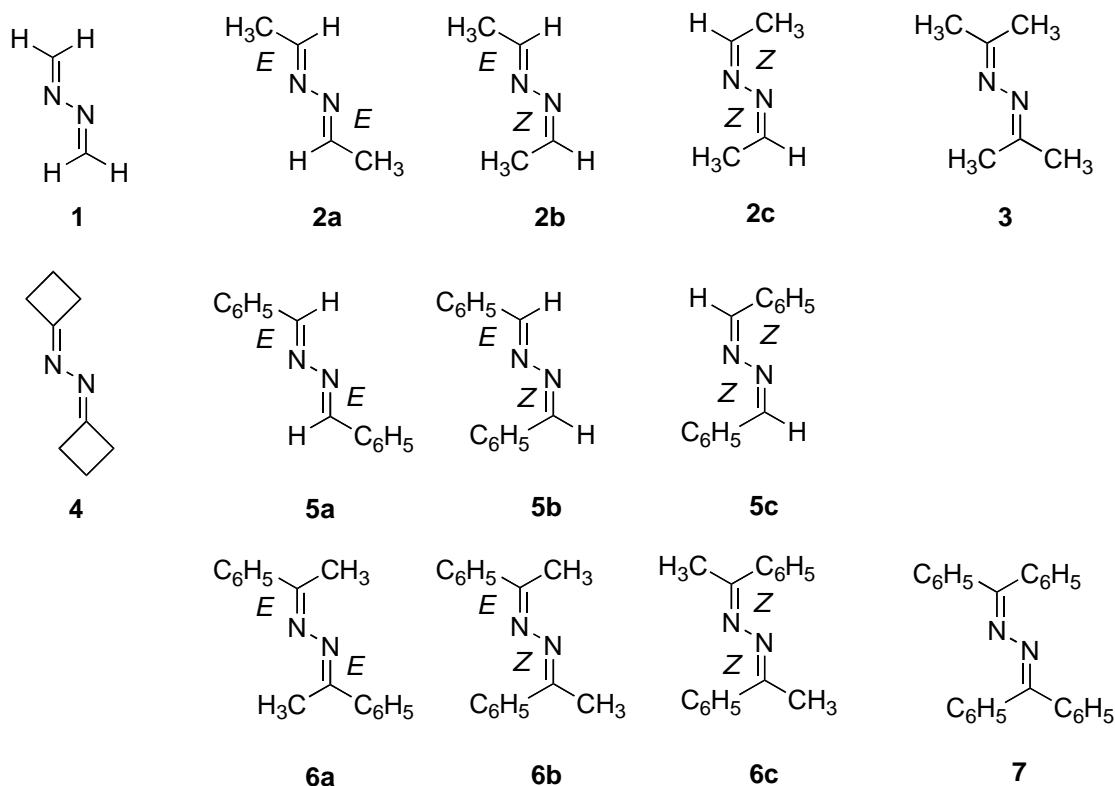


II



III

This ambiguity makes the search in databases more difficult. Some of us published in the past several papers devoted to azines in the second meaning of the definition (from now on the word azine will be restricted to compounds **II** and **III**).¹ Azines have been the subject of several studies with special emphasis on their use as synthons,^{1i,1j,2} on their mesogenic (as such or with metals, metallomesogens) and NLO properties,³ as well as for their interesting structural properties.⁴ Formaldazine **1** occupies a special position and it is frequently considered a diazabutadiene.⁵ In this first paper devoted to azines, we will report the results obtained with compounds **1–7** (Scheme 1).



Scheme 1. Aldazines (**1**, **2**, **5**) and ketazines (**3**, **4**, **6**, **7**).

For aldazines **II** (compounds **2** and **5**) and for these ketazines **III** where $R \neq R'$ (compound **6**) three configurational isomers are possible: the *E,E* (**a**), the *E,Z* (**b**) and the *Z,Z* (**c**). All of them have been calculated.

Computational details

The optimization of the geometries and the calculation of frequencies (to evaluate the minimum nature of the geometries obtained) of the structures were first optimized at the B3LYP/6-31G* and then reoptimized at the B3LYP/6-311++G** computational level⁶⁻⁸ within the Gaussian-03

package.⁹ The directly calculated frequencies were scaled by a factor of 0.9613¹⁰ to account for the overestimation of vibrational frequencies at the B3LYP/6-31G* level.

Results and Discussion

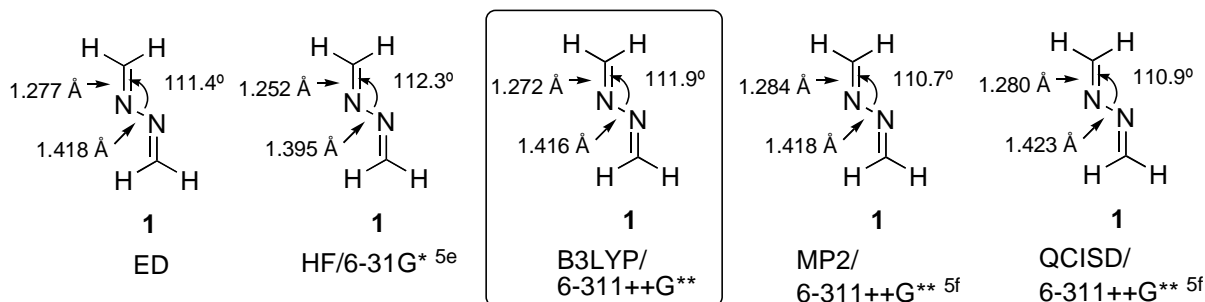
Geometries

The geometries of the C=N–N=C fragments are reported in Table 1.

Table 1. Geometries (Å, °), absolute energies (Hartree), relative energies (kJ mol⁻¹) and dipole moments (D)

Azine	C3-N1	N1-N2	N2-C4	C3N1N2	N1N2C4	C3N1N2C4	E	E _{rel}	μ
1	1.272	1.416	1.272	111.9	111.9	180.0	-188.1053	----	0.0
2a	1.275	1.411	1.275	112.4	112.4	180.0	-266.7761	0.0	0.0
2b	1.279	1.411	1.276	114.4	111.8	180.0	-266.7728	8.8	0.7
2c	1.278	1.386	1.278	116.3	116.3	135.8	-266.7700	16.2	1.8
3	1.284	1.395	1.284	115.4	115.4	153.0	-345.4358	----	1.16
4	1.270	1.414	1.270	112.3	112.3	177.8	-421.5902	----	0.08
5a	1.284	1.391	1.284	112.6	112.6	180.0	-650.3495	0.0	0.0
5b	1.287	1.383	1.284	117.6	113.2	154.3	-650.3415	21.1	1.7
5c	1.286	1.354	1.286	121.0	121.0	130.4	-650.3367	33.5	2.2
6a	1.290	1.371	1.290	117.3	117.3	142.9	-729.0017	0.0	1.2
6b	1.291	1.376	1.291	116.6	117.8	151.4	-728.9963	14.0	1.2
6c	1.290	1.376	1.290	118.2	118.2	150.9	-728.9904	29.6	1.2
7	1.295	1.371	1.295	117.0	117.0	153.6	-1112.5579	---	0.8

The structure of **1** has been determined by electron diffraction^{5d} and then calculated (HF/6-31G*) by Bachrach and Liu.^{5d,e} A comparison of these structures with that reported in Table 1 is represented in Scheme 2. The superiority of the B3LYP/6-311++G** calculations is evident. Only MP2 and QCISD gave comparable results.^{5f}



Scheme 2. The geometry of 2,3-diaza-1,3-butadiene (formaldazine). ED stands for the experimentally determined (Electron Diffraction) geometry

The structures of the three azines of Scheme 1 (**5**, **6** and **7**) have been determined by X-ray crystallography.

Table 2. Geometries (Å, °) of benzalazines **5**, **6** and **7**

Azine	C3-N1	N1-N2	N2-C4	C3N1N2	N1N2C4	C3N1N2C4
5a	1.284	1.391	1.284	112.6	112.6	180.0
5b	1.287	1.383	1.284	117.6	113.2	154.3
5c	1.286	1.354	1.286	121.0	121.0	130.4
BZAZIN02	1.275	1.417	1.275	111.8	111.8	180.0
BZAZIN11	1.269	1.413	1.269	112.6	112.6	180.0
6a	1.290	1.371	1.290	117.3	117.3	142.9
6b	1.291	1.376	1.291	116.6	117.8	151.4
6c	1.290	1.376	1.290	118.2	118.2	150.9
LIKHIW	1.278	1.403	1.278	115.4	114.5	138.7
LIKHIW01	1.285	1.396	1.286	115.6	114.4	139.7
7	1.295	1.371	1.295	117.0	117.0	153.6
ZOSLUO	1.286	1.404	1.286	116.4	116.4	132.5
ZOSLUO01	1.287	1.394	1.287	116.4	116.4	130.0
ZOLUO02	1.294	1.395	1.294	116.4	116.4	129.8

Three aspects are worth discussing:

1) The calculated geometries are similar to the experimental ones; in general, the azadiene system is more delocalized in the calculations than in the X-ray structures. The NN/NC ratios are: 1.083 (**5a**) vs. 1.114 (BZAZIN11); 1.063 (**6a**) vs. 1.086 (LIKHIW01), and 1.059 (**7**) vs. 1.078 (CCDC 299197). The angles are well reproduced and the important torsion angle is identical in **5a** (planar), a little lower (less flat) in LIKHIW01 compared with **6a** (ratio 0.98) and clearly lower in ZOSLUO (average of three structures) compared with **7** (ratio 0.85). These increased deformation from the plane are probably crystal-packing effects.

2) We have used Taft Steric parameter E_s (0 for H, -1.24 for CH_3 and -3.72 for C_6H_5).¹¹ Although the correlations were not satisfying, the torsion angle only depends on the internal substituents. There is also a significant relationship between the torsion angle and the angles at the N atoms (the average in the case of non-symmetric compounds): torsion angle = $875 - 6.2$ NNC angle, $r^2 = 0.82$.

3) In the case of **4**, the ring strain localized the azadiene conjugated system. If we compare **3** with **4**, the NN/NC ratios are 1.086 and 1.113, respectively. The torsion angle is very different, 153° for **3** and 178° for **4**, due to the less steric demand of the methylene groups of the four

membered rings. This azine (CAS RN **72593-07-8**), first prepared in 1953,^{12a} has only been described twice.^{2k,12b}

4) Compounds **1** and **3** have been calculated at the MP2/6-31G* level by Kobychew *et al.*^{5g} Their geometries are similar to those we have reported in Table 2. Besides, they have calculated the energy curve about the N–N bond rotation.

Infrared and Raman C=N stretchings.

The normal mode frequencies and corresponding vibrational assignments have been carried out theoretically at the B3LYP/6-31G* level. Raman and infrared stretchings of compounds of Scheme 1. In general, the symmetric vibrations are observed in the Raman spectra while the asymmetric ones in the infrared one. In Figure 1 we have reported the case of acetaldazine **2a**.

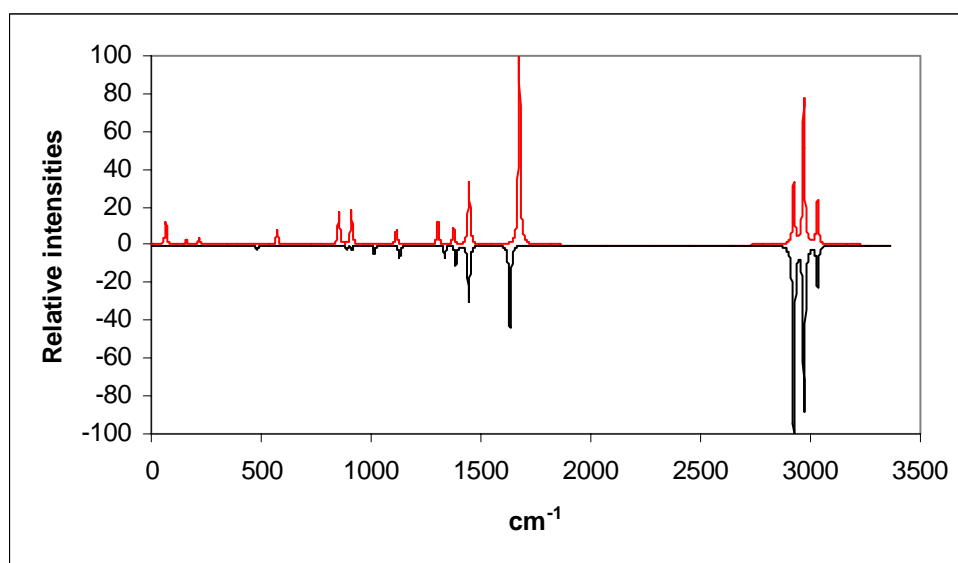


Figure 1. Infrared (up in red) and Raman (down in black) calculated stretchings of **2a**: relative intensities and band positions (in cm^{-1}).

The experimental study of this compound (pure liquid, both IR and Raman) has shown that the molecule has a C_{2h} symmetry, *i.e.* either **2a** or **2c**.^{1g} Theoretical calculations prove that **2a** is more stable than **2c** (Table 1).

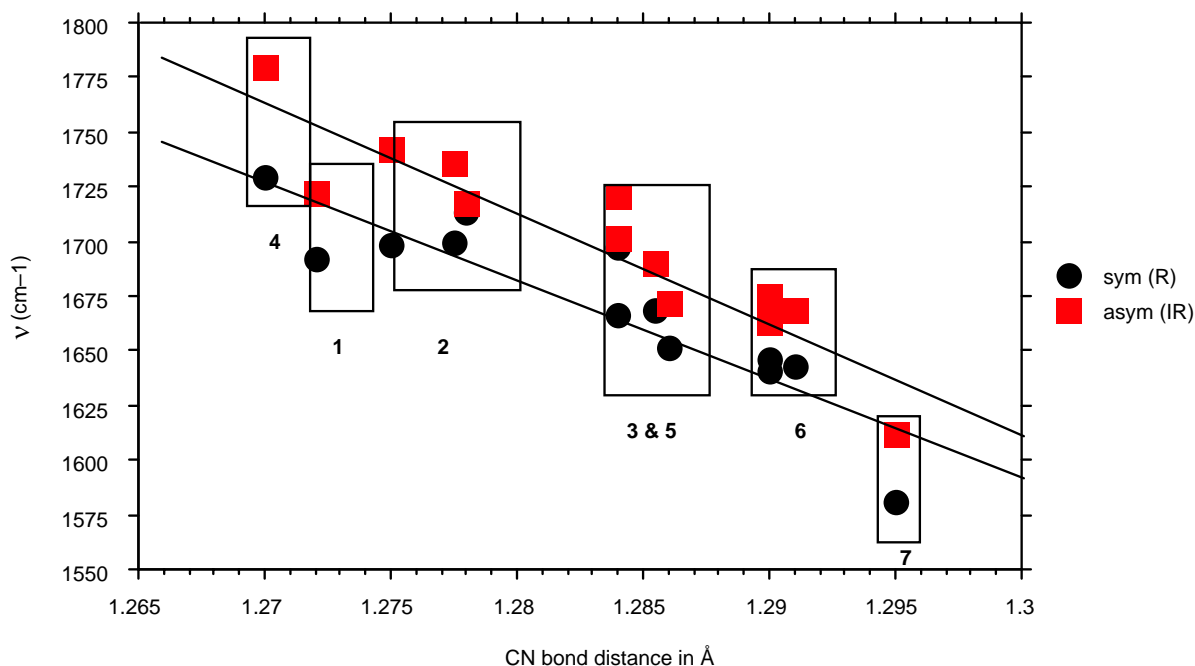


Figure 2. Symmetric (Raman, black) and antisymmetric (IR, red) stretchings (ν , cm^{-1}) of the $>\text{C}=\text{N}-\text{N}=\text{C}<$ fragments of azines **1** to **7** against the corresponding CN bond distance (\AA).

In Figure 2 we have plotted the calculated stretchings vs. the calculated CN distances. The extreme positions are occupied by cyclobutanone azine **4** and benzophenone azine **7**. The C=N stretching band of azines **2a** and **5a** has been reported by Frederickson.¹³ They appear at 1651 (liquid) and 1625 (CHCl_3 solution). According to our calculations (gas phase) they should appear at 1674.5 and 1636.2 cm^{-1} .

Energies

The relative energies of Table 1 can be discussed using Taft's steric effects or a presence absence matrix (Free-Wilson). In the first case we obtained $E_{rel} = 7.1 - 3.5 E_s (Z) + 1.5 E_s (E)$, $n = 9$, $r^2 = 0.92$ and in the second one $E_{rel} = 12.0 - 4.9 \text{ Me} (E) + 1.2 \text{ Me} (Z) - 6.3 \text{ Ph} (E) + 12.5 \text{ Ph} (Z)$, $n = 9$, $r^2 = 0.97$. Both equations are similar and correspond to the fact that substituents in the Z position destabilize the compound (more for the bulkier Ph than the smaller Me) whereas in the E-position the effects are just the opposite.

We have already shown that in the solid state the isomers present are **5a** (BZAZIN) and **6a** (LIKHIW). In solution, the barriers to E/Z isomerization about the C=N bond are weak enough for the equilibrium to be reached immediately.^{1d} Experiments at 60 MHz with pure compounds have established that in the case of benzalazine only **5a** is present in solution (that means that less than 2% of the other isomers could be present) while in the case of acetaldazine, the mixture was 85% of **2a**-15% of **2b** (**2c** not observed, *i.e.* less than 2%).^{1f} A 85/15 mixture corresponds at

300 K to a difference of 4.3 kJ mol⁻¹, which is in reasonable good agreement with the results Table 1 taking into account that the differences in dipole moments are weak. In the case of **5**, isomer **5b** lies 21.1 kJ mol⁻¹ higher in energy than **5a**.

Conclusions

This paper reports the first attempt to theoretically study azines (with the exception, mentioned above, of formaldazine **1**). Geometries, *E/Z* isomerism and vibrational aspects have been computed, being in reasonable agreement with experimental data, when available.

Acknowledgements

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