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Synthesis and structural studies of symmetric and unsymmetric adamantylmethyleneazines

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ABSTRACT: The synthesis and spectroscopic properties (^{1}H, ^{13}C and ^{15}N NMR, in solution and in the solid state) of six new 1-adamantylmethylene azines are reported. The crystal and molecular structures of 1-adamantylcarbaldehyde azine and 1-adamantyl methyl ketone azine, which exist in the solid state in the *E*,*E*-configuration, were determined by x-ray analysis. The geometric characteristics of the azine central bridge and the preferred configuration with regard to it (*E*,*E*, *E*,*Z* or *Z*,*Z*) were investigated by means of the crystallographic data retrieved from the Cambridge Structural Database and *ab initio* quantum chemical calculations. Copyright © 1999 John Wiley & Sons, Ltd.

KEYWORDS: Adamantylmethyleneazines; x-ray structures; *ab initio* calculations; multinuclear magnetic resonance; cross-polarization magic angle spinning NMR

INTRODUCTION

Azines are 2,3-diazabutadiene derivatives that can also be viewed as N—N-linked diimines. They have been widely studied as a part of heterocyclic compounds[1,2] and recently are receiving increasing attention for their biological, chemical and physical properties.[3–5] On the other hand, the adamantyl group has been successfully used to stabilize certain functional groups, and the high crystalline character of adamantyl compounds provides an additional advantage in the product isolation procedure.[6] Moreover, the pharmacodynamic effects of the adamantyl group are closely related to its highly lipophilic character and compact symmetrical architecture.[7] On these bases, the aim of our work has been the synthesis and stereochemical structural studies of the symmetric and unsymmetric adamantylmethyleneazines **1**–**6** (Scheme 1).

The conformation of the N—N bond in these azines can be s-*cis*, s-*trans*, both planar, or s-*gauche* and, for unsymmetric azines, there are four possible configurations, *E*,*E*, *E*,*Z*, *Z*,*E* and *Z*,*Z* (Scheme 2). The s-*cis* conformation is obviously destabilized owing to strong interactions of the vicinal electron lone pairs, electrostatic effects and steric repulsion of the two *endo* substituents, a reason why non-protonated azines undergo criss-cross cycloaddition instead of [4 + 2] cycloaddition.[3] In azines, the *gauche* conformation is destabilized by alkyl substitution in favour of the s-*trans* form, which is usually the only conformer detected by spectroscopic methods.[8]

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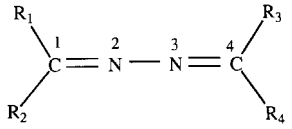
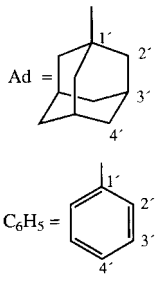
EXPERIMENTAL

General methods. Melting-points were determined on a

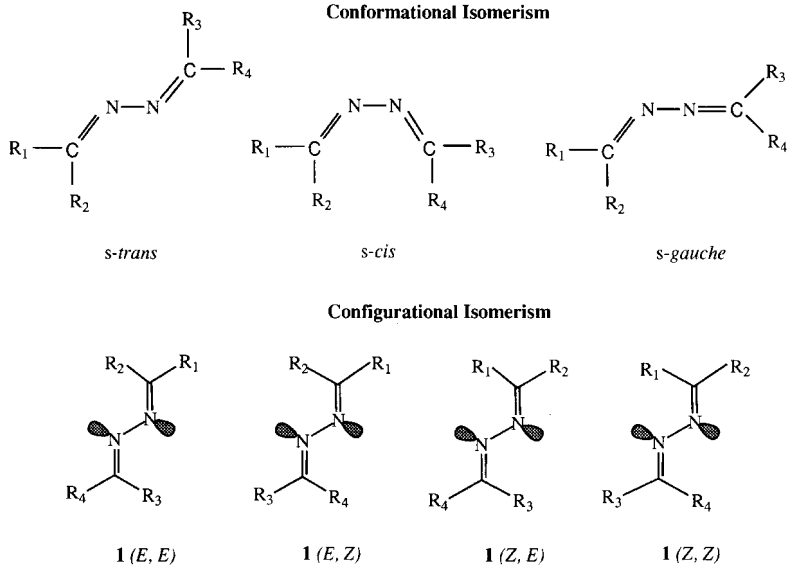


Compound	R_1	R_2	R_3	R_4
1	H	Ad	H	Ad
2	CH_3	Ad	CH_3	Ad
3	H	Ad	CH_3	Ad
4	H	Ad	C_6H_5	C_6H_5
5	CH_3	Ad	C_6H_5	C_6H_5
6	CH_3	Ad	H	-HC=CH-C_6H_5



Scheme 1

CCC 0894–3230/99/060455–15 $17.50



Scheme 2

hot-stage microscope and are uncorrected. Analytical thin-layer chromatography was performed on Merck $60F_{254}$ silica gel with a layer thickness of 0.2 mm. Combustion analyses were performed with a Perkin-Elmer model 2400 CHN instrument. NMR spectra were obtained on Bruker AC-200 and DRX-400 instruments. The ^{1}H and ^{13}C chemical shifts (δ, ppm) are given relative to external tetramethylsilane. ^{15}N NMR spectra are referred to nitromethane as external standard; no corrections for bulk differences were applied.[9] Solid-state ^{13}C cross-polarization magic angle spinning (CP/MAS) NMR spectra were obtained with a Bruker AC200 spectrometer using the experimental conditions already described.[10]

Compounds. 1-Bromoadamantane, 1-adamantyl methyl ketone (**9**), (*E*)-cinnamaldehyde (**11**) and benzophenone (**12**) are commercial products. Benzophenone hydrazone (**13**) was obtained from benzophenone and hydrazine, according to the literature.[11]

*1-Adamantylcarbaldehyde (**7**).* This compound was synthesized by the Bouveault reaction[12] starting from dry 1-bromoadamantane (1.07 g, 5.0 mmol), anhydrous *N*,*N*′-dimethylformamide (5.2 mmol), 10.5 mmol of 25% lithium dispersion in mineral oil or lithium wire (both containing 1% sodium; with a lesser amount of Na, e.g. 0.05%, the reaction did not work)[13] in 50 ml of anhydrous THF under argon and external cooling with ultrasonic radiation from a Virsonic 300 Model 175893 Cell Disrupter (20 kHz), the reaction being completed at room temperature in 5 min (lithium dispersion)–50 min (lithium wire) (the reaction was followed by thin-layer chromatography). The excess of lithium was filtered and the traces of it remaining in the reaction mixture were destroyed with ammonium chloride in an ice-bath to prevent heating of the solution. The solution was then extracted with diethyl ether or dichloromethane and the solvent evaporated off.

Filtration over dry silica gel 60 (230–400 mesh) using hexane separates the unreacted 1-bromoadamantane and high-R_f secondary products and elution with hexane–ethyl acetate (75:25) affords pure 1-adamantylcarbaldehyde (**7**) (yields 50–75%), m.p. 160–162 °C (lit. m.p. 139–141 °C[14] and 195–197.3 °C[15]), R_f = 0.52 in hexane-diethyl ether (9:1). IR (KBr): ν(C=O) = 1720 cm^{-1}. The ν(C=O) band shifts to a lower value, 1670 cm^{-1}, when the 1-adamantylcarbaldehyde (**7**) is not completely pure, so the IR technique is a useful tool to determine its purity.

*1-Adamantylcarbaldehyde azine (**1**).* To a solution of 35 mg (1.1 mmol) of anhydrous hydrazine in 4 ml of ethanol, 328.8 mg (2 mmol) of 1-adamantylcarbaldehyde (**7**) in 10 ml of ethanol were added with external cooling. The reaction mixture was stirred at 0 °C for 30 min. Azine **1**, m.p. 217–218 °C (chloroform–propan-2-ol or hexane), yield 90%, $C_{22}H_{32}N_2$ (M_r 324.5). Analysis: calculated C 81.43, H 9.95, N 8.63; found C 81.31, H 9.65, N 8.75%.

When using 2 ml of anhydrous hydrazine and 103 mg (0.63 mmol) of 1-adamantylcarbaldehyde in 2 ml of ethanol and after 1 h of reaction at room temperature, the 1-adamantylcarbaldehyde hydrazone (**8**) was isolated, containing a 9% of **1**. Upon standing in the solid state for 24 h, the hydrazone **8** was completely converted into azine **1**.

Labelled [$^{15}N_2$]-1-adamantylcarbaldehyde azine (**1**) was similarly prepared from 1-adamantylcarbaldehyde

(**7**) (27.4 mg, 0.167 mmol) and [$^{15}N_2$]hydrazine sulphate in 5 ml of ethanol at room temperature for 18 h.

*1-Adamantyl methyl ketone azine (**2**).* Refluxing, for 4 h, a solution of 1-adamantyl methyl ketone (**9**) (1.79 g, 10 mmol) and anhydrous hydrazine (0.33 g, 10.3 mmol) in 40 ml of ethanol gave 1.53 g (yield 86%) of 1-adamantyl methyl ketone azine (**2**), m.p. 206–208 °C (chloroform–propan-2-ol), $C_{24}H_{36}N_2$ (M_r 338.5). Analysis: calculated C 81.74, H 10.31, N 7.95; found C 81.72, H 9.97, N 7.92%.

By reacting 2 g (11.2 mmol) of 1-adamantyl methyl ketone (**9**) in 12 ml of ethanol with 8 ml of anhydrous hydrazine at room temperature for 18 h, 2.09 g (yield 97%) of 1-adamantyl methyl ketone hydrazone (**10**) were formed, m.p. 74.5–76.5 °C. Attempts to crystallize **10** from hexane yielded the azine **2** as the only product.

*Azine **3**.* Reaction of 1-adamantyl methyl ketone hydrazone (**10**) (192.3 mg, 1 mmol) with 1-adamantylcarbaldehyde (**7**) (164.4 mg, 1 mmol) in 10 ml of ethanol at room temperature for 1 h yielded azine **3**, m.p. 132–133.5 °C (chloroform–methanol) (yield 90%), $C_{23}H_{34}N_2$ (M_r 338.5). Analysis: calculated C 81.60, H 10.12, N 8.28; found C 81.20, H 10.19, N 8.08%.

*Azines **4** and **5**.* These azines were obtained by refluxing for 2 h in ethanol solution benzophenone hydrazone (**13**), with stoichiometric amounts of 1-adamantylcarbaldehyde (**7**) and 1-adamantyl methyl ketone (**9**), respectively. Azine **4:** m.p 104–105 °C (hexane), yield 90%, $C_{24}H_{26}N_2$ (M_r 342.5). Analysis: calculated C 84.17, H 7.65, N 8.18; found C 83.91, H 7.37, N 8.33%. Azine **5:** m.p 126–128 °C (ethanol), yield 83%, $C_{25}H_{28}N_2$ (M_r 356.5). Analysis: calculated C 84.22, H 7.92, N 7.86; found C 83.88, H 8.21, N 7.84%.

*Azine **6**.* To 1-adamantyl methyl ketone hydrazone (**10**) (0.576 g, 3.0 mmol) in 25 ml of ethanol, 0.40 g (3.03 mmol) in ethanol of (*E*)-cinnamaldehyde (**11**) were added. The yellowish reaction mixture was stirred for 1 h at room temperature, then the solvent was evaporated off and the crude material was quickly chromatographed on silica gel 60 (70–200 mesh) with chloroform as eluent. $R_f = 0.5$, m.p 63.5–65.7 °C, yield 75%, $C_{21}H_{26}N_2$ (M_r 306.5). Analysis: calculated C 82.31, H 8.55, N 9.14; found C 82.23, H 8.30, N 9.44%.

It must be noted that the unsymmetrical azine **6** readily evolved to a mixture of 1-adamantyl methyl ketone azine (**2**) and (*E*)-cinnamaldehyde azine.

*Crystal structure determination of compounds **1** and **2**.* Crystals of **1** and **2** were obtained from hexane and chloroform–propan-2-ol, respectively. A summary of the data collection and the refinement process is given in Table 1. The temperature of the crystals was controlled using an Oxford Cryostream Cooler.[16] The structures were solved by direct methods (SIR92)[17] and refined by least-squares procedures on F_{obs}. All hydrogens atoms were obtained from difference Fourier synthesis and refined isotropically in the last cycles of the refinement. The weighting schemes were established as to give no trends in $\langle \omega\Delta^2 F\rangle$ vs $\langle F_0\rangle$ and $\langle \sin\theta/\lambda\rangle$.

The structure of **3** (Scheme 1) has not been determined since it is pseudoisomorphous with that of **2** [same symmetry and analogous cell parameters: $a = 6.8895(4)$, $b = 21.0538(29)$, $c = 6.8299(6)$ Å and $\beta = 101.255(7)°$]. The scattering factors were taken from the *International Tables for X-Ray Crystallography*.[18] The calculations were carried out with the XTAL,[19] PESOS[20] and PARST[21] set of programs running on a DEC200 workstation. The atomic coordinates of **1** and **2** have been deposited (CSD 101729 and 101730, respectively).

Theoretical calculations. The *ab initio* calculations, without any geometrical restrictions, were performed using the Gaussian94 program.[22]

RESULTS AND DISCUSSION

Chemistry

The symmetrical azines **1** and **2** were prepared by reacting 1-adamantylcarbaldehyde (**7**)[12] and 1-adamantyl methyl ketone (**9**) with hydrazine in ethanol solution, according to Scheme 3. As will be discussed later, the azines have an *E*,*E*-configuration, which is consistent with the steric demands of the substituents at the azine-C atoms.

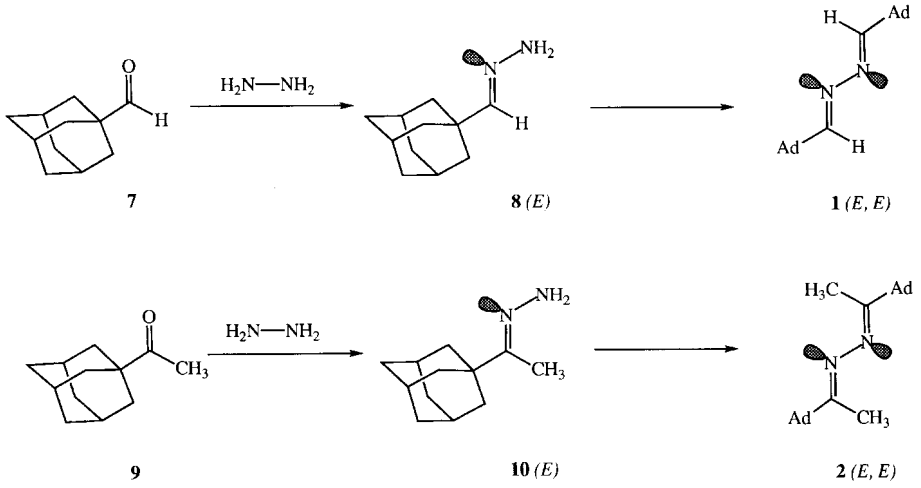
Formation of hydrazones **8** and **10** was observed when an excess of hydrazine was employed. 1-Adamantyl methyl ketone hydrazone (**10**) is fairly stable, but 1-adamantylcarboxaldehyde hydrazone (**8**) readily converts into the azine **1** upon standing in the solid state after 24 h and in ethanol solution after 20 min. In $(CD_3)_2SO$ at 373 K after 10 h and in CD_3OD at 323 K after 16 h there are mixtures of **1** and **8** in ratios of 60:40 and 80:20, respectively. 1-Adamantylcarbaldehyde hydrazone (**8**) does not change in $CDCl_3$ solution in 1 week, but after 10 months in a refrigerator a mixture of **1** and **8** (66:34) is obtained.

We assume that the azine **1** is formed, in solution during the synthesis or in the solid state, from two molecules of hydrazone **8** by a classical addition–elimination mechanism, addition of a hydrazone to another hydrazone with elimination of hydrazine (Scheme 4),[3d] but it remains to be explained why the reaction is so fast in the solid state, even when the hydrazone C=N group is sterically hindered owing to the bulky adamantyl group.

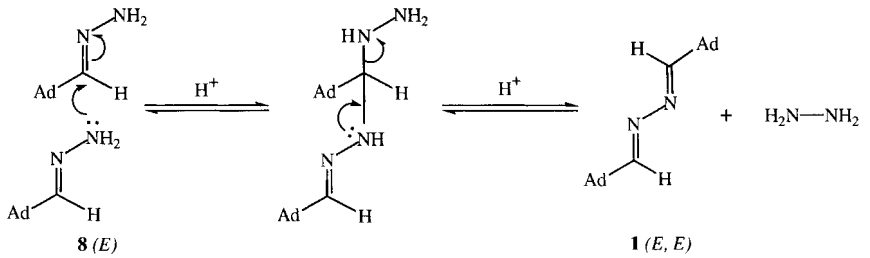
In the case of the sterically hindered 1,1′-biadamantyl ketone, all attempts to obtain the corresponding hydrazone and/or azine proved to be unsuccessful, e.g. by

Table 1. Crystal analysis parameters

	1	2
Crystal data		
Formula	$C_{22}H_{32}N_2$	$C_{24}H_{36}N_2$
Crystal habit	Colourless, plate	Colourless, prism
Crystal size (mm)	0.67 × 0.30 × 0.07	0.50 × 0.33 × 0.17
Symmetry	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/n$
Unit cell determination:	Least-squares fit from 66 reflections (θ <45°)	Least-squares fit from 64 reflections (θ <45°)
Unit cell dimensions (Å, °)	a = 12.1439(8)	a = 6.9996(3)
	b = 6.8156(3)	b = 20.7149(15)
	c = 12.5173(7)	c = 6.7400(3)
	α = 90	α = 90
	β = 116.221(4)	β = 99.392(4)
	γ = 90	γ = 90
Packing: V (Å^3), Z	929.4(1), 2	964.2(1), 2
D_c(g cm^{-3}), M, F(000)	1.160, 324.5, 356	1.214, 352.6, 388
μ (cm^{-1})	5.05	5.24
Experimental data		
Technique	Four-circle diffractometer, Philips PW1100, bisecting geometry; graphite oriented monochromator; $\omega/2\theta$ scans; detector apertures 1 × 1°; 1 min per reflection; Cu Kα; θ_{max} = 65; scan width = 1.5°	
Number of reflections:		
Independent	1575	1642
Observed [2σ(I)criterion]	1405	1518
Standard reflections	2 reflections every 90 min; no variation	
Temperature (K)	200	200
Solution and refinement:		
Solution	Direct methods: Sir92	
Refinement:		
Least-squares on F_o	Full matrix	
Secondary extinction ($\times 10^4$)	0.27(4)	0.64(5)
Parameters:		
Number of variables	174	191
Degrees of freedom	1231	1327
Ratio of freedom	8.08	7.95
Final shift/error	0.0004	0.004
H atoms	From difference synthesis	
Weighting scheme	Empirical so as to give no trends in $\langle\omega\Delta^2F\rangle$ vs $\langle\lvert F_{obs}\rvert\rangle$ and $\langle\sin\theta/\lambda\rangle$	
Max. thermal value (Å^2)	U33[C13] = 0.051(1)	U33[C3] = 0.0391(1)
Final ΔF peaks (e Å^{-3})	0.25	0.24
Final R and Rw	0.038, 0.045	0.041, 0.051



Scheme 3



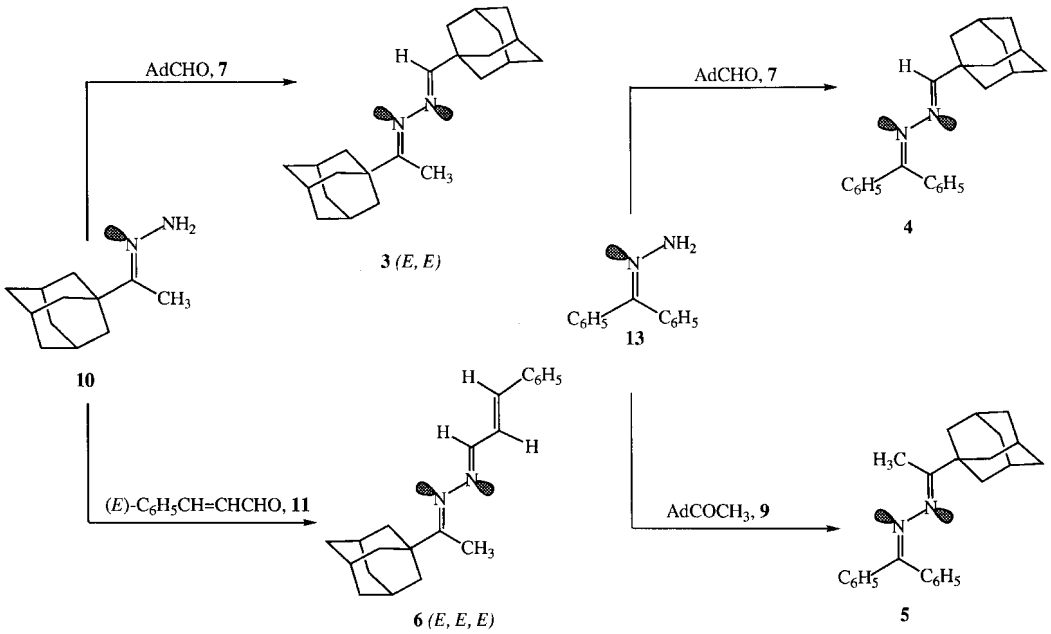
Scheme 4

reflux with hydrazine in ethanol without an acid catalyst or in acid conditions (hydrochloric or sulphuric acids) or by microwave irradiation in open vessels or under pressure.

The unsymmetric azines **3** (*E*,*E*) and **6** (*E*,*E*,*E*) were prepared in quantitative yields from 1-adamantyl methyl ketone hydrazone (**10**) and 1-adamantylcarbaldehyde (**7**) or (*E*)-cinnamaldehyde (**11**), respectively. (Scheme 5). To obtain azines **4** and **5**, the starting material was the benzophenone hydrazone **13**, which in turn was formed by refluxing in ethanol for 24 h a stoichiometric mixture of benzophenone and hydrazine (Scheme 5).[11]

X-ray crystallography

The molecular structures of 1-adamantylcarbaldehyde azine (**1**) and 1-adamantyl methyl ketone azine (**2**) were determined by x-ray analysis, proving that they exist in the solid state in the *E*,*E*-configuration. Both compounds present a crystallographic centre of symmetry relating the two halves of the molecule, therefore only half a molecule is in the asymmetric unit. The introduction of a methyl group in **2** mainly affects the geometry around the atom to which it is attached (Table 2 and Fig. 1): a lengthening of the N1—C2 and C2—C4 bonds and a narrowing of the N1—C2—C4 angle together with an opening of the C2—C4—C5/C12 angles are observed. The N1=C2 bond length presents a double bond character, mainly in **1**, in agreement with the standard[23] C_{sp^2}=N distance of 1.279 Å and the N1—N1′ length is greater than the tabulated value[23] for the (C)(C,H)—N—N—(C)(C,H) of 1.401 Å with planar N atoms. Azines **1** and **2** have an s-*trans* *E*,*E*-configuration and the adamantyl group in an almost eclipsed disposition with respect to the N1 atom (N1—C2—C4—C11 close to 0°). They retain the same conformation at the expense of the bond lengths and angular distortions mentioned above as a clear effect of the methyl substituents to lessen the steric interactions. A related effect is that one CH_2 group



Scheme 5

Table 2. Experimental intra- and intermolecular geometric parameters (Å, °) [a]

	1	**2**		**1**	**2**
N1—C2	1.264(2)	1.280(2)	C4—C5	1.540(2)	1.543(2)
N1—N′	1.428(2)	1.426(2)	C4—C11	1.531(2)	1.541(2)
C2—C3	—	1.504(2)	C4—C12	1.544(2)	1.549(2)
C2—C4	1.496(2)	1.521(2)	⟨C—C⟩	1.531(1)	1.533(1)
C2—N1—N1′	111.6(1)	112.9(1)	C2—C4—C11	113.0(1)	112.0(1)
N1—C2—C4	123.7(1)	117.2(1)	C2—C4—C12	108.7(1)	109.4(1)
N1—C2—C3	—	124.1(1)	C2—C4—C5	108.5(1)	110.3(1)
C4—C2—C3	—	118.7(1)	⟨C—C—C⟩	109.5(1)	109.5(1)
C2—N1—N1′—C2′	180.0(1)	180.0(1)	C2—C4—C11—C10	−179.7(1)	179.3(1)
N1′—N1—C2—C3	—	−0.1(2)	C2—C4—C12—C8	177.2(1)	178.8(1)
N1′—N1—C2—C4	−179.5(1)	−179.3(1)	C2—C4—C5—C6	−178.0(1)	−178.1(1)
N1—C2—C4—C5	−125.7(1)	−126.0(1)	⟨C—C—C—C⟩	59.9(1)	59.7(1)
N1—C2—C4—C12	117.1(2)	114.7(1)			
N1—C2—C4—C11	−4.4(2)	−5.2(2)			

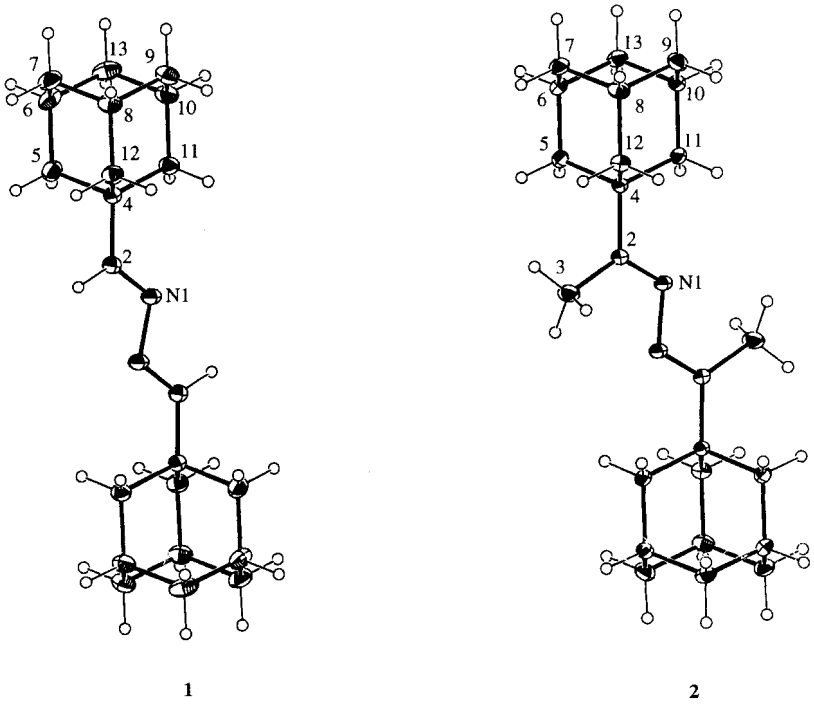
Interactions	D—H	D···A	H···A	D—H···A
1: C13—H132···N1(*x*,*y*−1,*z*)	1.03(2)	3.680(2)	2.89(2)	134(2)
2: C13—H131···N1(*x*,*y*,*z*−1)	0.98(2)	3.683(2)	2.93(2)	135(2)

[a] ⟨ ⟩ represents the average value for the geometry of the adamantanyl group. Dashes stand for the (1−*x*, 1−*y*, 1−*z*) and (1−*x*,−*y*, 1−*z*) symmetry operations in **1** and **2** respectively.

of the adamantyl moiety is closer in **2** to the N1 nitrogen lone pair, the C11···N1 distance in **2** being significantly shorter than in **1** [2.701(2) vs 2.821(2) Å].

The central C═N—N═C fragment and the H3 or C3 substituents are in the same plane (χ^2 = 0.81 in **1** and 0.63 in **2** vs the tabulated value of 7.81[21]), whereas the C4 atom deviates by 0.012(1) and 0.018(1) Å, respectively. As expected, the four six-membered rings of the conformationally rigid adamantyl groups adopt an undistorted chair conformation following the Cremer and Pople parameters.[21]

In order to analyse the geometric characteristics of the azine central unit, 51 molecules corresponding to 49 structures (neutral organic compounds without errors, *R*-



1 **2**

Figure 1. Molecular structures of compounds **1** and **2** showing the numbering system and the 30% displacement ellipsoids

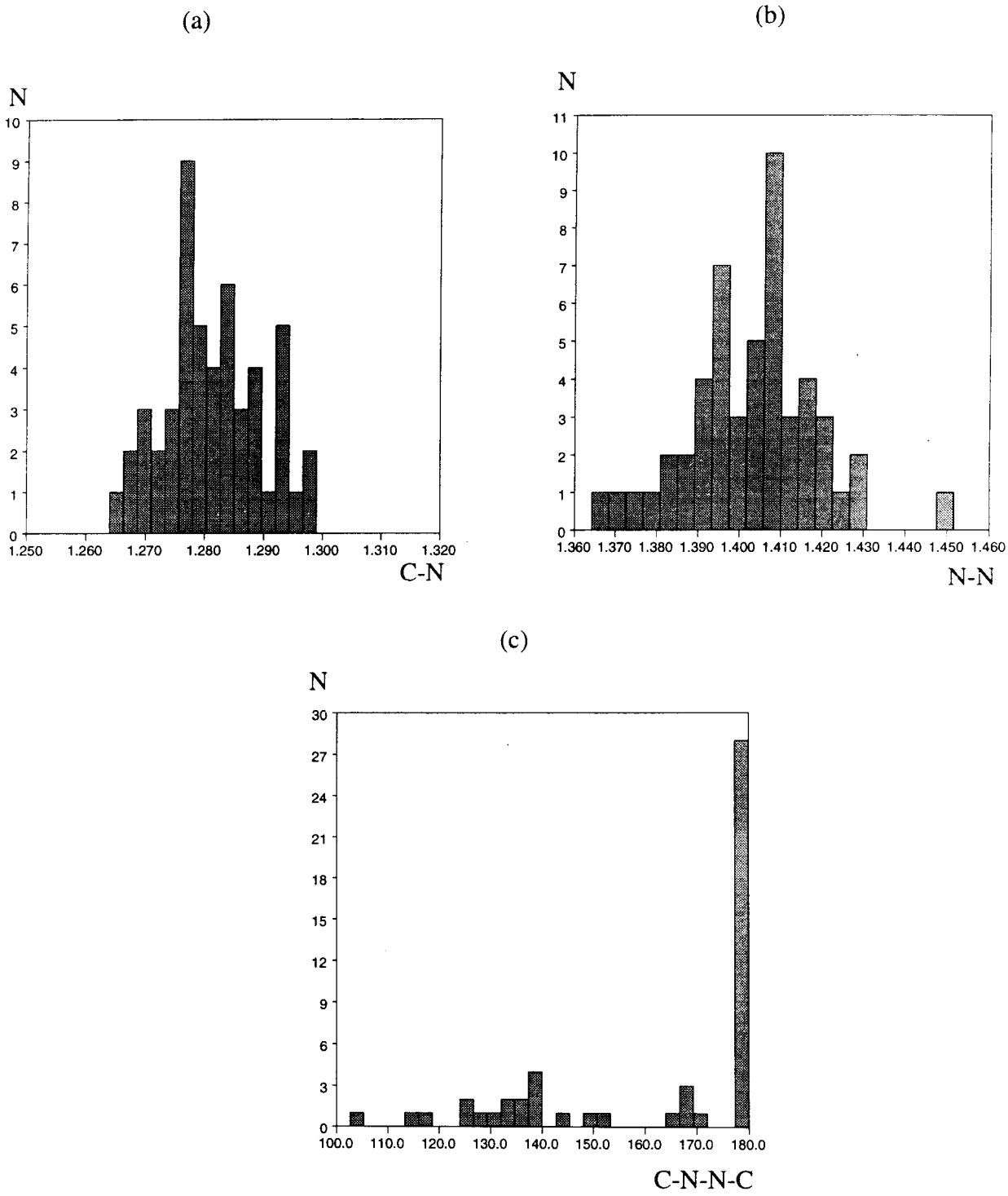


Figure 2. Histograms of (a) the C—N and (b) the N—N bond lengths and (c) the C—N—N—C torsion angle corresponding to the retrieved structures containing the azine central unit

factor<10% and with substituents at the end of the fragment, R_1 to R_4 = H, C, not belonging to a ring were retrieved from the Cambridge Structural Database (CSD) (October 1997 release).[24] It was found that 41 out of 49 structures present an *E*,*E*-configuration in coincidence with azines **1** and **2**, two (FEHBUP, JULHAZ) have an *E*,*Z*-configuration although a polymorphic form of the last one [(*E*,*Z*)-2-nitroacetophenone azine] exists in the *E*,*E*-form (JULGUS), and the remaining structures present a *Z*,*Z*-configuration. Figure 2(a)–(c) show the histograms of the N—N and C—N distances and the C—N—N—C torsion angle. The corresponding average

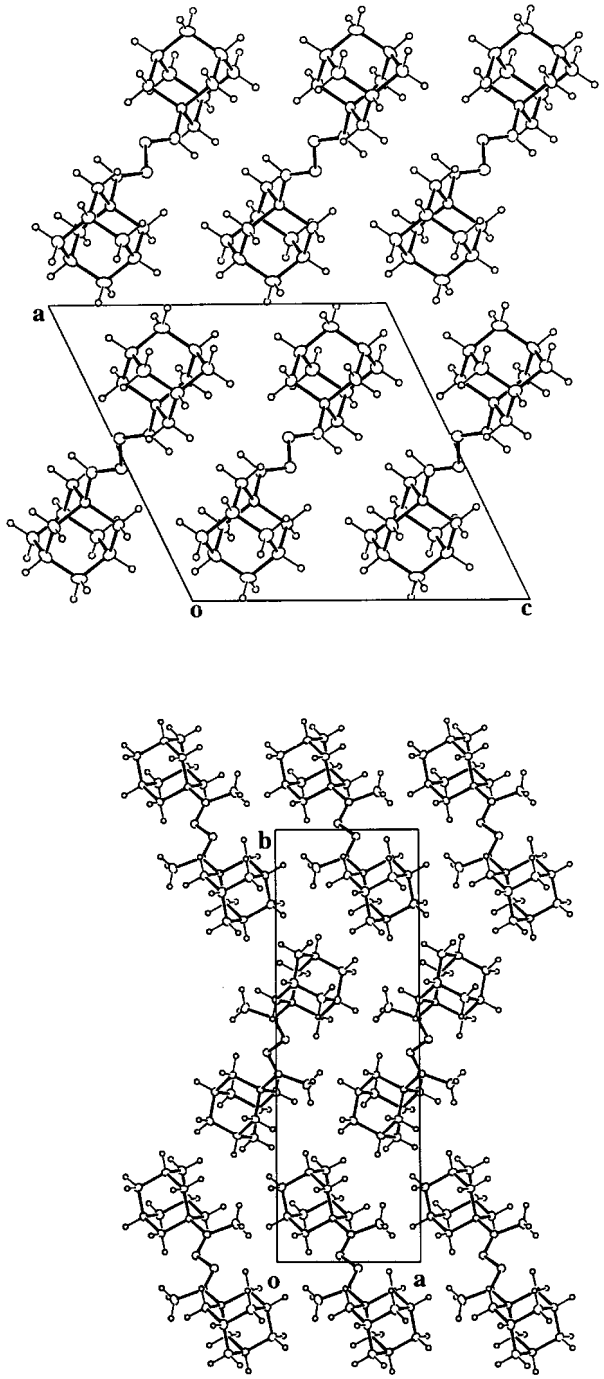


Figure 3. Crystal packing of compounds **1** and **2** showing the similar dispositions of the adamantyl groups in adjacent layers

values with the standard deviation of the sample in parentheses are 1.403(15), 1.282(8) Å and 162(24)°. 2,5-Diacetyl-3,4-diazahexa-2,4-diene (FIFHUX)[8b] is located in the lower end of the (a) and (c) histograms. This molecule has a *gauche* conformation [C—N—N—C = 102.7(2)°] and a partial double bond character in N=N [1.368(4) Å], but the C—N distance [1.282(3) Å] is coincident with the average value of the histogram (a). The upper end of the N—N bond distances (1.448 Å) is due to 4,4′-dibromobenzalazine (BRBZAL), and its C—N distance (1.276 Å) is close to the standard value of the C_{sp^2}=N bond distance. The minimum value of 1.266 Å in the C=N distribution is found in 4-trifluoromethoxybenzalazine (LACGUR), for which the N—N bond distance (1.417 Å) is in the upper end of its range. The C—N—N—C histogram [Fig. 2(c)] shows a maximum at 180.0°, only 18 molecules have a torsion angle smaller than 160.0° and five are in between the *gauche* and *trans* conformations (range 166.2–169.4°). From the analysis of the structures contributing to each part of the histogram, we can conclude that all the aldazines are *trans* and the cetazines can be either *trans* or *gauche* (AACFAZ10 and SACFAZ10 are stereoisomers, both *E,E* although the former presents a central torsion angle of 180.0° and the latter 114.7°).

1-Adamantylcarbaldehyde azine (**1**) and 1-adamantyl methyl ketone azine (**2**) show N—N distances in the upper end of the histogram, reflecting a marked single bond character. In **1**, the C—N bond distance approaches the minimum value of the distribution whereas in **2** it is close to the average.

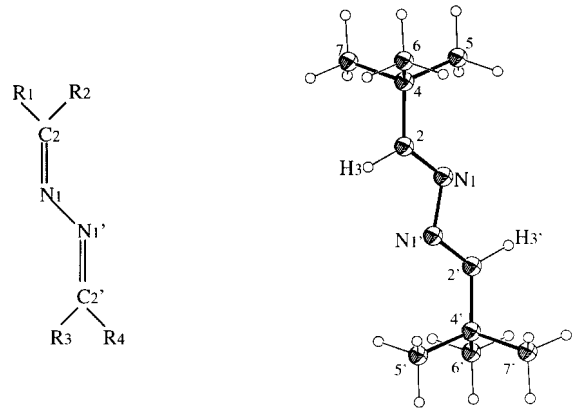
The molecules are grouped in layers, those of **2** being disposed in a herringbone fashion (Fig. 3). Within each layer, the molecules are related by a screw axis in **1**, whereas in **2** they are related by a translation along the **a** direction. In both compounds, the adamantyl groups of adjacent layers are facing to each other keeping analogous C9···C7 distances between them [4.002(2) and 3.947(2) Å in **1** and **2**, respectively]. Only weak[25] C—H···N intermolecular interactions (Table 1) relate molecules along the **b** and **c** directions. There are no voids[26] in the crystal structure and the total packing coefficients amount to 0.66 and 0.69.

Ab initio calculations

Owing to the different configurational possibilities present in azines, and also those observed in the structures retrieved from the CSD, theoretical calculations at the *ab initio*[22] level were undertaken on some simple compounds. Previous *ab initio* studies of azines were limited to formaldazine (**14**); the potential hypersurface of this compound was calculated by Bachrach and Liu[27] at the MP2/6–31G*//HF/6–31G* level. Other azines have been calculated using semi-empirical methods.[8b,c]

We start with two 'symmetrical' azines devoided of configurational isomerism, formaldazine (**14**) and acetone azine (**15**), and then we proceed with the study of the *E,E*-, *E,Z*- and *Z,Z*-configurations of acetaldazine (**16**). Moreover, taking into account the size of the adamantyl

Table 3. Calculated molecular geometry (Å, °) by *ab initio* methods at the HF/6–31G* level (energy in hartree)



Compound:	**14**	**15**	**16**			**17**		
R1 = R4:	H	CH_3	CH_3			$C(CH_3)_3$		
R2 = R3:	H	CH_3	H			H		
			E,E	*E,Z*	*Z,Z*	*E,E*	*E,Z*	*Z,Z*
N1—C2	1.253	1.262	1.255	1.256	1.258	1.255	1.256	1.259
N1—N1′	1.395	1.390	1.394	1.393	1.391	1.395	1.394	1.390
N1′—C2′	1.253	1.262	1.255	1.258	1.258	1.255	1.258	1.259
C2—N1—N1′	112.3	114.0	112.7	112.2	114.6	112.7	111.8	115.6
C2′—N1′—N1	112.3	114.0	112.7	115.1	114.6	112.7	116.4	115.6
N1—C2—C4/H4	118.4	117.6	121.4	121.5	129.5	123.4	123.9	131.9
N1′—C2′—C4′/H4′	118.4	117.6	121.4	129.4	129.5	123.4	131.9	131.9
C4—C2—N1—N1′	—	180.0	180.0	180.0	0.0	180.0	180.0	0.0
C4′—C2′—N1′—N1	—	180.0	180.0	0.0	0.0	180.0	0.0	0.0
C2—N1—N1′—C2′	180.0	180.0	180.0	180.0	180.0	180.0	180.0	180.0
C5—C4—C2—N1	—	—	—	—	—	−0.1	0.1	61.5
C6—C4—C2—N1	—	—	—	—	—	121.0	121.2	−61.5
C7—C4—C2—N1	—	—	—	—	—	−121.1	−121.0	180.0
C5′—C4′—C2′—N1′	—	—	—	—	—	0.1	61.5	61.5
C6′—C4′—C2′—N1′	—	—	—	—	—	121.2	−61.5	−61.5
C7′—C4′—C2′—N1′	—	—	—	—	—	−120.9	180.0	180.0
E(RHF)[a]	−186.8860	−343.0536	−264.9756	−264.9722	−264.9688	−499.1831	−499.1740	−499.1651
ΔE(kcal mol^{-1})	—	—	0.0	2.1	4.3	0.0	5.7	11.3

[a] 1 hartree = 627.5095 kcal mol^{-1}.

group, the geometry of the azine **17** with *tert*-butyl groups at C2 was also optimized as a model for **1**.

Concerning the geometry of the C═N—N═C fragment, as the substituents change from hydrogen to *tert*-butyl, the N1—C2—C/H bond angle increases. Formaldazine (**14**) has been examined in the gas phase by IR, Raman spectroscopy and electron diffraction (ED) techniques, suggesting a dominant *trans* conformation.[28] Its C═N and N—N bond lengths [1.277(2) and 1.418(3) Å] are longer than those calculated in the present study, and the C—N—N bond angle [111.4(2)°] is smaller if the HF method is considered, but they agree fairly well when methods that take into account electron correlation effects are used (Table 4) (note that Bachrach and Liu[27] geometries being calculated at the HF/6–31G* level are identical with ours for **14** in Tables 3 and 4). Since MP2 and B3LYP calculations are of comparable quality and owing to the computer time consumed by MP2 calculations for the azines under study, only the HF and B3LYP methods were applied to **15** and **17**. Acetone azine (**15**) has been thoroughly investigated in the gaseous, liquid and crystalline states and it was concluded that only one configuration exists in the different physical states.[29] There is an experimental value for acetaldazine (**16**) [d_{NN} = 1.437(13)Å] determined by ED[30] which is probably overestimated (1.41–1.42 Å would be more consistent with both calculations for **16** and experimental values for other azines in Table 4).

Concerning the stereochemistry of the C═N bonds in azines, the ED data[30] for acetaldazine (**16**) showed that

Table 4. Experimental and theoretical calculations at different levels for the *E*,*E*-isomers of azines: energies (*E*, hartree)[a] and geometries (Å,°)

Compound	R_1	R_2	Method	*E*	N—C	N—N	C—C	CNN	HCN/CCN	CNNC
			HF/6–31G*[b]	−186.886	1.253	1.395	—	112.3	118.4	180.0
14	H	H	MP2/6–31G*	−187.457	1.287	1.431	—	109.9	117.7	180.0
			B3LYP/6–31G*	−188.048	1.276	1.423	—	111.1	118.0	180.0
			ED[18]	—	1.277(2)	1.418(3)	—	111.4(2)	120.7(8)	Not reported
			HF/6–31G*[b]	−264.976	1.255	1.394	1.496	112.7	121.4	180.0
16	Me	H	MP2/6–31G*	−265.809	1.290	1.425	1.491	110.5	120.3	180.0
			B3LYP/6–31G*	−266.698	1.279	1.417	1.495	111.6	121.1	180.0
			ED[20]	—	1.277(3)	1.437(13)	1.486(8)	110.4(9)	121.4(10)	Not reported
15	Me	Me	HF/6–31G*[b]	−343.054	1.262	1.390	1.504	114.0	117.6	180.0
			B3LYP/6–31G*	−345.338	1.288	1.406	1.506	114.3	116.3	180.0
17	Bu^t	H	HF/6–31G*[b]	−499.183	1.255	1.395	1.511	112.7	123.4	180.0
			B3LYP/6–31G*	−502.581	1.278	1.418	1.511	111.8	123.0	180.0
1	Ad	H	XR (this work)	—	1.264(2)	1.428(2)	1.496(2)	111.6(1)	123.7(1)	180.0(1)
2	Ad	Me	HF/6–31G*	−1038.710	1.263	1.390	1.526	114.4	118.0	179.3
			XR (this work)	—	1.280(2)	1.426(2)	1.521(2)	112.9(1)	117.2(1)	180.0(1)

[a] 1 hartree = 627.5095 kcal mol^{-1}.
[b] From Table 3.

Table 5. ^{1}H NMR chemical shifts (ppm) and coupling constants (*J*, Hz) of azines **1–6** and hydrazones **8**, **10** and **13**

Compound	Solvent	R_1/R_3		R_2/R_4	
1[a]	$CDCl_3$	7.53	2.02 (6H)	1.69/1.75 (12H) ^2J = 12.6	1.75 (12H)
2	$CDCl_3$	1.63	2.03 (6H)	1.69/1.74 (12H) ^2J = 12.0	1.82 (12H)
3	$CDCl_3$	1.81 7.10	2.03 (6H)	1.65–1.80 (12H) ^2J[b]	1.80 (6H) 1.76 (6H)
4	$CDCl_3$	7.41	1.98 (3H)	1.65/1.72 (6H) ^2J = 12.2	1.65 (6H)
		C_6H_5 = 7.61–7.63 (2H−*o*); 7.24–7.27 (2H−*o*); 7.33–7.41 (2H−*p* + 4H−*m*)			
	CD_3OD	7.31	1.94 (3H)	1.65/1.72 (6H) ^2J = 11.8	1.62 (6H)
		C_6H_5 = 7.17–7.58(m)			
5	$CDCl_3$	1.82	1.97 (3H)	1.62/1.70 (6H)	1.64 (6H)
		C_6H_5 = 7.66–7.69 (2H−*o*); 7.19–7.21 (2H−*o*); 7.34–7.39 (2H−*p* + 4H−*m*)			
6	$CDCl_3$	1.93	2.06 (3H)	1.71/1.77 (6H) ^2J = 12.2	1.84 (6H)
		7.96 ^3J = 9.1	C_6H_5 = 7.50 (d, 2H, H−*o*); 7.36 (t, 2H, H−*m*); 7.31 (t, 1H, H−*p*) —HC=CH— = 7.04 (dd, ^3J = 16.0, ^3J = 9.1), 6.94 (d, ^3J = 16.0)		
	CD_3OD	1.90	2.05 (3H)	1.75/1.81 (6H) ^2J = 12.5	1.86 (6H)
		7.90 ^3J = 9.0	C_6H_5 = 7.55 (d,2H, H−*o*); 7.38 (t,2H, H−*m*); 7.32 (t, 1H, H−*p*) —HC=CH— = 7.01 (dd, ^3J = 16.0, ^3J = 9.0), 7.10 (d, ^3J = 16.0)		
8	$CDCl_3$	6.86 5.0 (NH_2)	1.99 (br, 3H)	1.67/1.73 (6H) ^2J = 12.4	1.66 (6H)
	DMSO−d_6	6.76 5.79 (NH_2)	1.93 (br, 3H)	1.61/1.68 (6H) ^2J = 12.0	1.57 (6H)
10	$CDCl_3$	1.68 4.86 (NH_2)	2.01 (br, 3H)	1.67/1.73 (6H) ^2J = 13.2	1.72 (6H)
13	$CDCl_3$	5.44 (NH_2)	7.46–7.54 (m, 5H)	7.26–7.32 (m, 5H)	

[a] $^2J(^5N)$ = +2.9, $^3J(^{15}N)$ = −6.0.
[b] Not measurable.

the *E,E*-isomer prevails in the vapour phase in accordance with the computed results in which the *E,Z*- and the *Z,Z*-isomers are about 2.1 and 4.3 kcal mol^{-1}, respectively, less stable than the *E,E*-isomer (Table 3). The effect is more marked with the bulkier *tert*-butyl group; thus, in *tert*-butylcarbaldehyde azine (**17**), the relative energies are 0.0 (*E,E*), 5.7 (*E,Z*) and 11.3 (*Z,Z*). Note that the *E,Z*-isomer lies, in both cases, in the middle of the *E,E*- and *Z,Z*-isomers, as if both halves were independent. The difference between methyl and *tert*-butyl groups is due essentially to the difference in steric effects of these groups (Taft's E_s values are 0.00, −1.24 and −2.78, for H, CH_3 and *t*-C_4H_9, respectively).[31] Therefore, for R_1 = 1-adamantyl and R_2 = H (**1**) and for R_1 = 1-adamantyl and R_2 = CH_3 (**2**), the observed predominance of *E,E*-isomers is justified on these grounds (Table 2).

The *tert*-butyl groups in **17** show the same disposition as that of the adamantyl group in **1** and **2** [N1—C2—C4—C11 torsion angle: experimental value −4.4(2), −5.2(2)°, calculated value −0.1°). Finally we succeeded in minimizing the *E,E*-configuration of 1-adamantyl methyl ketone azine (**2**) at the HF/6–31G* level. The theoretical distances and torsional angles are in reasonably good agreement with the experimental values (Table 4), taking into account our previous comments about HF calculations.

Multinuclear magnetic resonance

The ^{1}H (Table 5), ^{13}C (Table 6) and ^{15}N (Table 7) NMR spectra were recorded for azines **1–6** and hydrazones **8, 10** and **13**. Assignment of the ^{1}H and ^{13}C NMR chemical shifts was achieved by comparison with the data obtained for the starting carbonyl compounds (Table 8) and by means of homonuclear and heteronuclear correlations.[32] The barriers to rotation about C=N bonds in azines are large enough to observe, by NMR at room temperature, the different *E/Z*-isomers when they occur.[8a] The results reported in Tables 5, 6 and 8 show the presence of only one isomer in solution. An interesting feature is that, for the same *C*-substituents, the chemical shift of the sp^2 carbon atom is always higher for azines than for hydrazones (between 6 and 16 ppm), a fact that can be used for identification.[33]

The ^{15}N NMR spectra of azines **1–6** present one nitrogen of imine type C=*N* in the range −27.7 to −33.9 ppm, except for the unsymmetrical azine **6** in

Table 6. ^{13}C NMR chemical shifts (ppm) and coupling constants (*J*, H_2) of azines **1**–**6** and hydrazones **8**, **10** and **13**

Compound	Solvent	R_1/R_3		R_2/R_4			C=N
1[a]	$CDCl_3$	—	36.7	39.6	27.9	36.7	170.9
				^1J = 128.9	^1J = 132.9	^1J = 126.0	^1J = 157.6
	CP/MAS	—	36.5	39.2	28.5	36.5	172.7
2	$CDCl_3$	11.4	40.2	39.7	28.3	36.9	164.4
		^1J = 127.5		^1J = 128.4	^1J = 133.7	^1J = 126.5	
	CP/MAS	12.6	41.0	39.2	28.5	37.4	174.2
3	$CDCl_3$	11.9	40.0	39.8	28.2	36.8	171.2
		^1J = 127.8		^1J = 127.8	^1J = 133.6	^1J = 127.2	
		—	36.9	39.6	28.0	36.7	164.3
				^1J = 127.8	^1J = 133.6	^1J = 127.2	^1J = 156.3
	CP/MAS	13.6	40.9	39.4	28.4	37.2	176.9
		—	37.2	39.4	28.4	37.2	168.6
4	$CDCl_3$	—	37.1	39.4	27.8	36.6	167.2
				^1J = 128.5	^1J = 131.4	^1J = 126.7	^1J = 158.4
			138.3	130.1	128.1	129.8	163.2
				^1J = 162.0	^1J = 162.0	^1J = 160.6	
						^3J = ^3J = 7.7	
			135.0	128.7	127.4	128.6	
				^1J = 160.1	^1J = 160.9	^1J = 160.1	
	CP/MAS	—	35.7	40.6/39.6	28.2/27.6	37.6/37.0	168.7/168.3
			139.7		130.6, 129.6, 127.9, 125.4		170.7/170.2
			138.1/137.7				
5	$CDCl_3$	13.1	40.1	39.4	28.2	36.8	165.5
		^1J = 127.5		^1J = 125.4	^1J = 132.9	^1J = 124.1	
			138.2	128.9	128.0	129.3	156.5
				^1J = 162.0	^1J = 160.0	^1J = 160.4	
				^3J = ^3J = 6.0	^3J = 7.2	^3J = ^3J = 7.7	
			135.2	128.2	127.6	128.4	
				^1J = 160.2	^1J = 161.7	^1J = 160.6	
				^3J = ^3J = 6.6	^3J = 6.6	^3J = ^3J = 7.4	
6	$CDCl_3$	12.4	40.3	39.6	28.3	36.8	173.5
		^1J = 128.0		^1J = 126.8	^1J = 130.7	^1J = 125.0	
			136.0	127.1	128.8	128.9	157.7
				^1J = 159.6	^1J = 160.6	^1J = 161.1	^1J = 160.6
					^3J = 7.5	^3J = ^3J = 7.4	^3J = 8.0
			—CH=CH—: 140.6 (C—C_6H_5, ^1J = 155.3);				
			126.0 (^1J = 158.6, ^3J = 10.3, ^2J = 3.8)				
	CP/MAS	12.4	39.7	39.7	28.2	37.0	171.5
			137.7	127.0/128.3	128.3/129.6	130.6	156.2
					—CH=CH—: 140.2; 124.0		
8	$CDCl_3$	—	36.7	40.1	28.1	36.7	155.0
				^1J = 129.4	^1J = 130.4	^1J = 126.0	^1J = 152.0
10	$CDCl_3$	8.9	39.7	39.5	28.2	36.7	157.9
		^1J = 125.9		^1J = 127.9	^1J = 133.2	^1J = 126.7	
	CP/MAS	8.8	39.8	41.1	29.4	37.4	154.7
13	$CDCl_3$	—	138.4	129.3	128.1	128.8	149.1
				^1J = 161.3	^1J = 160.2	^1J = 161.2	
		—	132.9	128.7	126.4	128.0	
				^1J = 160.5	^1J = 159.5	^1J = 160.3	

[a] $^1J(^{15}N) = 3.6$, $^2J(^{15}N) = 3.6$.

which the C=*N* conjugated with the cinnamyl residue appears at −16.6 ppm. Two nitrogen signals at around −60 ppm for the C=*N* and −276 ppm for the *N*H_2 in the (*E*)-hydrazones **8, 10** and **13** were observed.[34]

A sample of [$^{15}N_2$]-1-adamantylcarbaldehyde azine (**1**) was synthesized and studied by multinuclear NMR and the following characteristics typical of an *E*,*E*-isomer were observed: N, H couplings through two bonds, ^2J(*N*=C—*H*) = +2.9Hz and three bonds, ^3J(*N*—N=C—*H*) = −6.0Hz, and N,C coupling through one bond of 3.6 Hz and two bonds of also 3.6 Hz, calculated by a complete analysis with the WINDAISY 3.0 program using a ^1J(N,N) coupling constant of −11.7Hz.[34]

The ^{13}C and ^{15}N CP/MAS NMR of 1-adamantylcarbaldehyde azine (**1**) and 1-adamantyl methyl ketone azine (**2**), which we have proved by x-ray analysis exist as *E*,*E*-

Table 8. ^{1}H and ^{13}C NMR chemical shifts (ppm) and coupling constants (J, Hz) of the starting carbonyl compounds

Compound	Solvent	CH_3/CHO	C1′	H2′/C2′	H3′/C3′	H4′/C4′	CO	Other	
7	$CDCl_3$	9.31 (s, 1H)		1.72 (6H)	2.07 (br, 3H)	1.72 (6H)	—	—	
	CD_3OD	9.27 (s, 1H)		1.73 (6H)	2.05 (br, 3H)	1.82/1.74 (6H) ^{2}J = 12.2	—	—	
	$CDCl_3$	—	44.7	36.5 ^{1}J = 127.2	27.3 ^{1}J = 134.2	35.8 ^{1}J = 128.8	205.7 ^{1}J = 167.1	—	
9	$CDCl_3$	2.08 (s, 3H)		1.79 (br, 6H)	2.07 (br, 3H)	1.71 (6H)	—	—	
	$CDCl_3$	24.2 ^{1}J = 127.1	46.4	38.2 ^{1}J = 128.7	27.9 ^{1}J = 134.4	36.5 ^{1}J = 128.0	213.9	—	
	CP/MAS	22.7	46.7	38.4	29.1	37.0	210.5	—	
11	$CDCl_3$	9.71 (d, 1H) ^{3}J = 7.7		7.42–7.46 (m)	7.55–7.58 (m)	7.45(dd)	—	6.73 (dd, 1H)	7.48 (d, 1H) ^{3}J = 16.0
	CD_3OD	9.65 (d, 1H) ^{3}J = 7.8		7.48–7.41 (m)	7.71–7.62 (m)	7.48–7.41 (m)	—	6.77 (dd, 1H)	7.67 (d, 1H) ^{3}J = 15.0
	$CDCl_3$	—	133.8	128.9 ^{1}J = 162.6	128.3 ^{1}J = 159.9	131.1 ^{1}J = 161.5 ^{3}J = ^{3}J = 7.4	193.5 ^{1}J = 172.5 ^{3}J = 9.0	128.34 ^{1}J = 160.5	152.6 ^{1}J = 152.7 ^{3}J = ^{3}J = 4.6
12	$CDCl_3$	—	137.6	128.2	132.4	130.0	196.7	—	

Table 7. ^{15}N NMR chemical shifts (ppm) and coupling constants (*J*, Hz) of azines **1–6** and hydrazones **8, 10** and **13**

Compound	Solvent	N	N
1	$CDCl_3$	−27.7	−27.7
	CP/MAS	−20.8	−20.8
2	$CDCl_3$	−33.9	−33.9
	CP/MAS	−31.9	−31.9
3	$CDCl_3$	−31.4	−30.5
		$\Sigma J = 9.8$	$\Sigma J = 4.5$
4	$CDCl_3$	−29.2	−27.9
5	$CDCl_3$	−31.3	−28.4
6	$CDCl_3$	−28.9	−16.6
8	$CDCl_3$	−62.0	−275.1
		$^2J = 3.3$	^1J[a]
10	$CDCl_3$	−66.0	−281.1
		$\Sigma J = 6.1$	$^1J = 73.3$
13	$CDCl_3$	−59.7	−273.8
			$^1J = 77.9$

[a] Not observed.

isomers, show chemical shift values close to those obtained in solution, meaning that the only isomer detected in solution is the same as that found in solid state. A close examination of the CP/MAS NMR data for the remaining azines allows us to conclude that all of them (**1–6**) exist in the *E,E*-configuration in the solid state and in solution.

CONCLUSIONS

This work presents some novelties which can be summarized as follows: (i) for the first time adamantylmethyleneazines have been synthesized; these azines can be used as starting materials for preparing diazapentalenes (criss-cross cycloaddition reaction),[35] 2-pyrazolines[36] and many other heterocyclic compounds;[37] (ii) the first x-ray structures of azines bearing adamantyl groups have been reported; recently, there has been much interest in the structure of molecules containing an 1-adamantyl residue, such as Ad–CO–Ad[38] and Ad–NH–$COCH_3$,[39] related to the plasticity of adamantane and its derivatives;[40] (iii) A set of novel ^{13}C and ^{15}N chemical shifts, in solution and in the solid state, and also some ^{1}H–^{15}N and ^{13}C–^{15}N coupling constants were described.

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