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Nonempirical calculations of NMR indirect spin–spin coupling constants

Part 14†: Azomethines of the α,β-unsaturated aldehydes

Leonid B. Krivdin,[1,2]* Lyudmila I. Larina,[1] Kirill A. Chernyshev[1] and Alexander Yu. Rulev[1]

[1] A.E. Favorsky Irkutsk Institute of Chemistry, Siberian Branch of the Russian Academy of Sciences, Favorsky St 1, 664033 Irkutsk, Russia
[2] Department of Chemistry, Technical Academy of Angarsk, Tchaikovsky St 60, Angarsk 665835, Russia

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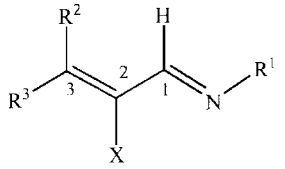
Configurational assignment of seven azomethines obtained from the α-functionally substituted and nonsubstituted α,β-unsaturated aldehydes has been performed on the basis of experimental measurements and the high-level *ab initio* calculations of their ^1J(C,C) and ^1J(C,H), involving the α-imino carbon that demonstrated the marked stereochemical dependence of both coupling constants upon the orientation of the nitrogen lone pair in the diverse isomers of the title azomethines. Copyright © 2005 John Wiley & Sons, Ltd.

KEYWORDS: NMR; spin–spin coupling constant; lone pair effect; SOPPA; configurational assignment; azomethines

INTRODUCTION

The double bond C═N is one of the most important functional groups in organic chemistry.[1] Numerous fundamental books and reviews are devoted to the different aspects of the carbon–nitrogen double bond chemistry. The interest in azomethines originated because of their remarkable properties. It is common knowledge that certain types of these derivatives are very important in the analysis of aldehydes and ketones. They are widely used in the preparation of different heterocyclic systems. Many of these azomethines serve as useful ligands in the synthesis of the metal coordinative compounds. Azomethine derivatives of the conjugated α,β-unsaturated aldehydes and ketones and especially their α-functionally substituted analogs are of particular interest because of their multifunctional reactivity. Thus, azomethinoenamines have been used as excellent ambident conjugated models for the solution of some problems of captodative aminoalkenes behavior.[2,3] Some aspects of the structural chemistry of the formyl- and azomethinoenamines have been discussed previously.[4]

In the present communication, configurational assignment of the seven azomethine derivatives of the α-functionally substituted and nonsubstituted α,β-unsaturated aldehydes **1–7** has been performed on the basis of experimental measurement and the high-level *ab initio* calculations of ^1J(C,C) and ^1J(C,H) involving the α-imino carbon, expectedly demonstrating the marked orientational nitrogen lone pair effect investigated in a number of our preceding papers.[5]



X = H, NR_2, OR, SR, Cl, Br; R^1, R^2, R^3 = H, Alk, Ph

1 - 7

RESULTS AND DISCUSSION

Identification and model structure

Signal assignment in the ^{13}C NMR spectra of the seven synthesized azomethines **1–7** (see Experimental part) was mostly straightforward while in the dubious cases it was justified by 'tracing out of carbon skeleton' by means of the sequential comparison of the corresponding ^1J(C,C) coupling constants. Configurational assignment at the C═N bond of **1–7** was performed as described in the next section by means of ^1J(C,C) and ^1J(C,H) involving the α-imino carbon measured via the INADEQUATE pulse sequence and accordingly, from the proton-coupled ^{13}C NMR spectra, as exemplified in Fig. 1. Additional configurational assignments at the C═C bond of **1** and **2** have been carried out on the basis of the values of ^3J(H,H) and ^3J(C,H) (which are characteristic for the *cis* and *trans* arrangements of the coupled nuclei) measured from the ^{1}H NMR and the

*Correspondence to: Leonid B. Krivdin, A.E. Favorsky Irkutsk Institute of Chemistry, Favorsky St 1, 664033 Irkutsk, Russia.
E-mail: krivdin@irk.ru
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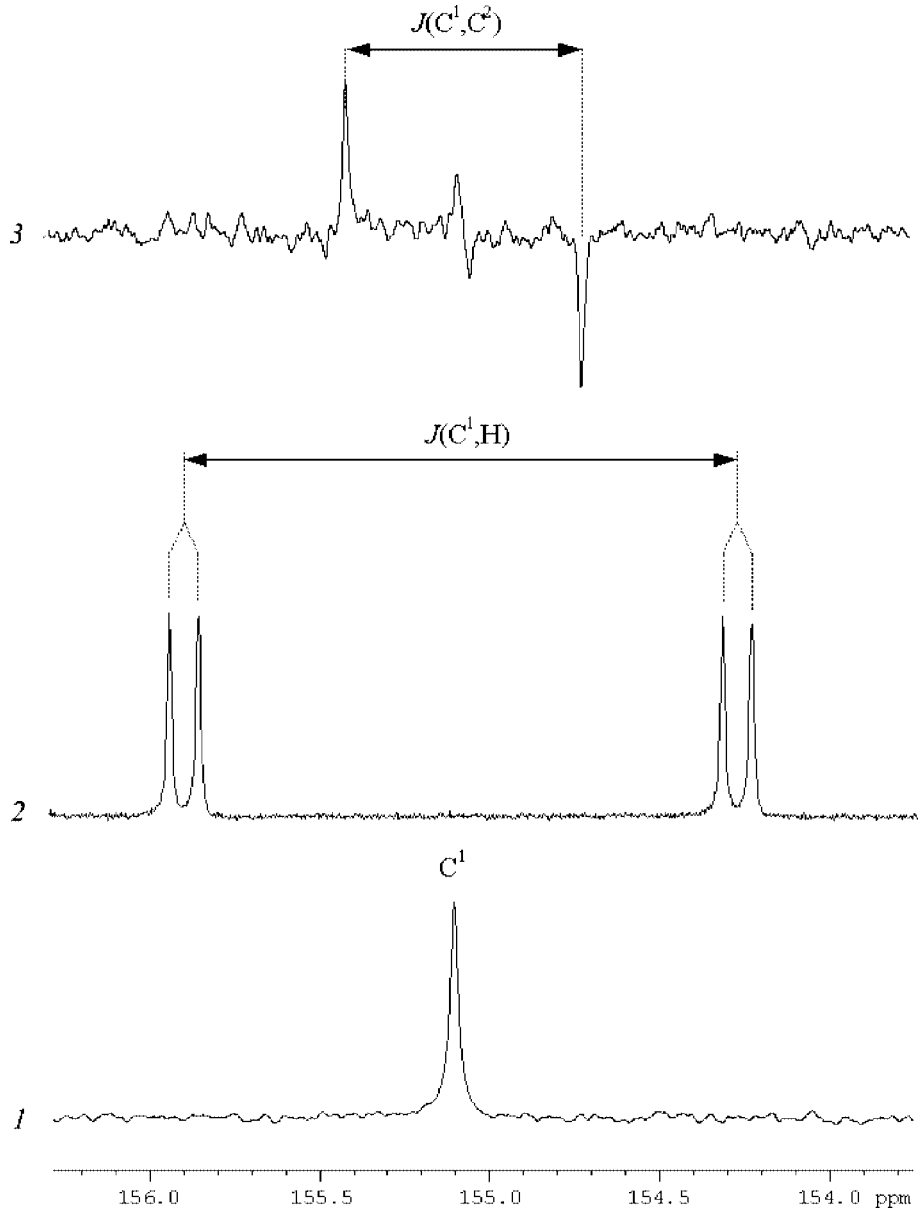


Figure 1. Lowfield region of the proton-decoupled (1), proton-coupled (2) and INADEQUATE (3) ^{13}C NMR spectra of **4** in $CDCl_3$ (101.61 MHz).

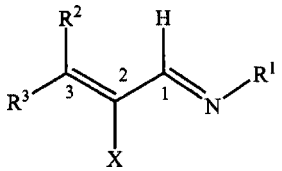
proton-coupled ^{13}C NMR spectra and by means of the complementary 2D NOESY experiments. The salient ^{13}C chemical shifts together with the ^{1}J(C,C) and ^{1}J(C,H) of **1–7** are given in Table 1.

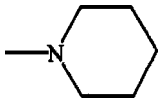
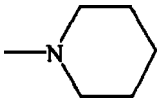
With a view to perform the desired configurational assignment at the C═N bond of **1–7**, we carried out a detailed theoretical study of six complementary model azomethines **8–13** since the compounds of the original series **1–7** were too large for the high-level *ab initio* calculations. The equilibrium conformations of the *Z* and *E* isomers of **8–13** located at the MP2/6-311G** level are shown in Figs 2–4.

Most of the model compounds **8–13** adopt predominant *s-trans* conformation, more favorable for the π,π conjugation in the C═C–C═N system; among these are **8** and **11** (both isomers), **9**(*E*), **10**(*Z*), **12**(*E*) and **13**(*E*). However, **9**(*Z*) and **12**(*Z*) represent equimolar (*ca* 50 : 50) equilibrium mixture of the *s-cis* and *s-trans* forms while **10**(*E*) and **13**(*Z*) adopt even predominant *s-cis* conformations. This implies that the *s-cis*/*s-trans* conformational equilibrium of the title azomethines depends upon the configuration at the C═N bond, and on the other hand, upon the nature of the substituent in the α-position of the alkenyl moiety and thus should be treated with care. This is why we were eager to get in the know whether the ^{1}J(C,C) and ^{1}J(C,H) involving the α-imino carbon (used here for the configurational assignment of the title azomethines **1–7**) provide conformational dependence in the studied series.

Almost all conformations in the model series **8–13** are ideally planar for both *E* and *Z* isomers in either *s-cis* or *s-trans* form. The only marked exception is the *Z* isomer of azomethine derivative of α-dimethylamino-α,β-unsaturated aldehyde (**9**): both *s-cis* and *s-trans* conformations of **9**(*Z*) demonstrate the marked out-of-plane deviation exceeding

Table 1. ^{13}C chemical shifts (δ, ppm) and the one-bond $^{13}C-^{13}C$ and $^{13}C-^{1}H$ spin–spin coupling constants (J, Hz) of **1–7** measured from the proton-decoupled, proton-coupled and INADEQUATE ^{13}C NMR spectra in $CDCl_3$ (101.61 MHz)



					^{13}C chemical shifts			Spin–spin coupling constants		
Cmpd	X	R^1	R^2	R^3	$\delta(C^1)$	$\delta(C^2)$	$\delta(C^3)$	$J(C^1, C^2)$	$J(C^2, C^3)$	$J(C^1, H)$
1	H	$(CH_2)_2OH$	H	Ph	164.77	129.28	142.40	62.5	70.5	156.6
2	H	$C(CH_3)_2CH_2OH$	H	Ph	159.15	130.05	141.13	63.5	70.2	156.3
3a		Me	H	Me	163.03	148.50	124.96	63.8	79.9	153.6
3b		Me	Me	H	158.60	147.80	111.44	66.7	78.3	155.6
4	OEt	*n*-Bu	H	H	156.75	156.71	92.30	[a]	80.5	159.7
5a	SBu	Me	H	Ph	164.11	134.07	131.01	62.8	75.1	158.3
5b	SBu	Me	Ph	H	159.63	137.28	131.26	61.4	75.7	162.4
6	Cl	*c*-Hex	Ph	Ph	155.10	129.92	148.76	70.0	83.0	163.7
7	Br	$SiMe_3$	H	Ph	158.68	122.69	141.51	69.3	[a]	166.8

[a] Not measured because of signals overlapping.

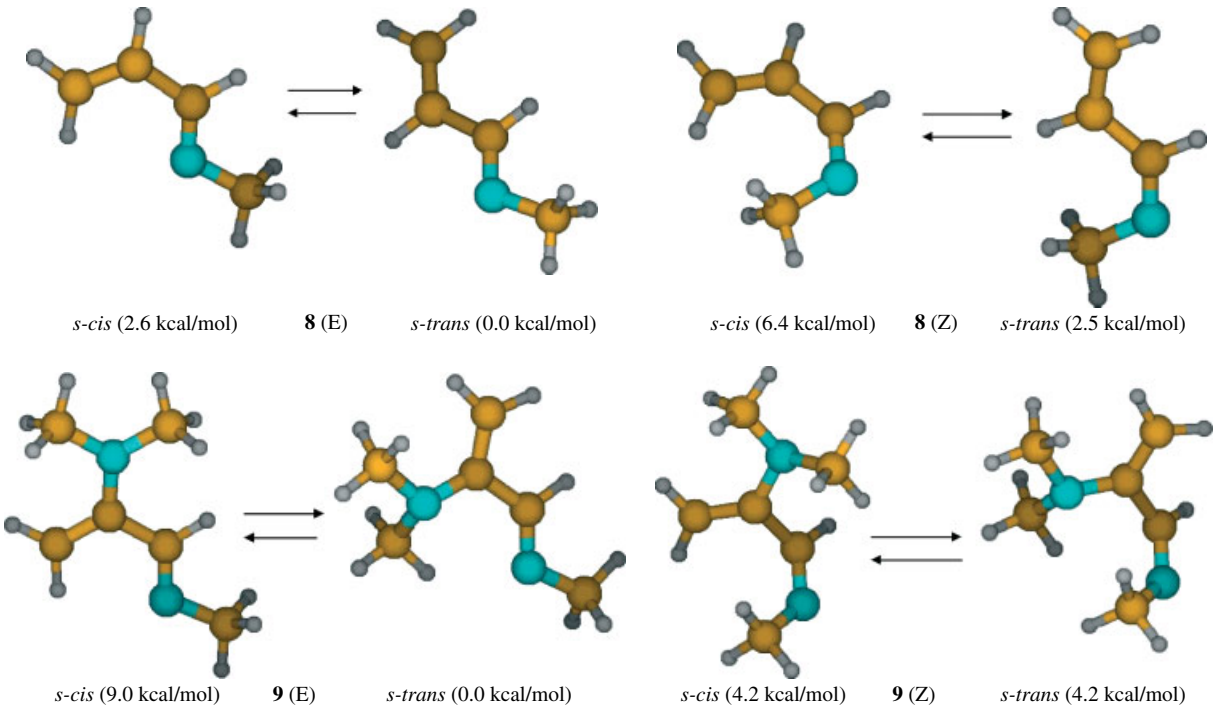


Figure 2. MP2/6–311G** optimized equilibrium conformations of *E* and *Z* isomers of the model azomethines (**8**) and (**9**). Relative energies are given in parentheses. Element colors: hydrogen – gray, carbon – yellow, nitrogen – cyan.

50° (54.5° in *s-cis* and 51.8° in *s-trans*). The diverse isomer **9**(*E*) is essentially planar in *s-cis* conformation and provides a minor out-of-plane deviation (10.9°) in the *s-trans* form. The noted out-of-plane deviations in **9** should be accounted for the intramolecular steric repulsion effects involving the hydrogen atoms of the dimethylamino group.

Configurational assignments

It was well established both in our early[6] and more recent[7] publications that in imines, the one-bond $^{1}J(C,C)$ demonstrate a profound stereochemical dependence on the orientation of the nitrogen lone pair. Indeed, the difference between J_{cis} and J_{trans} in imines amounts to 20% of their total

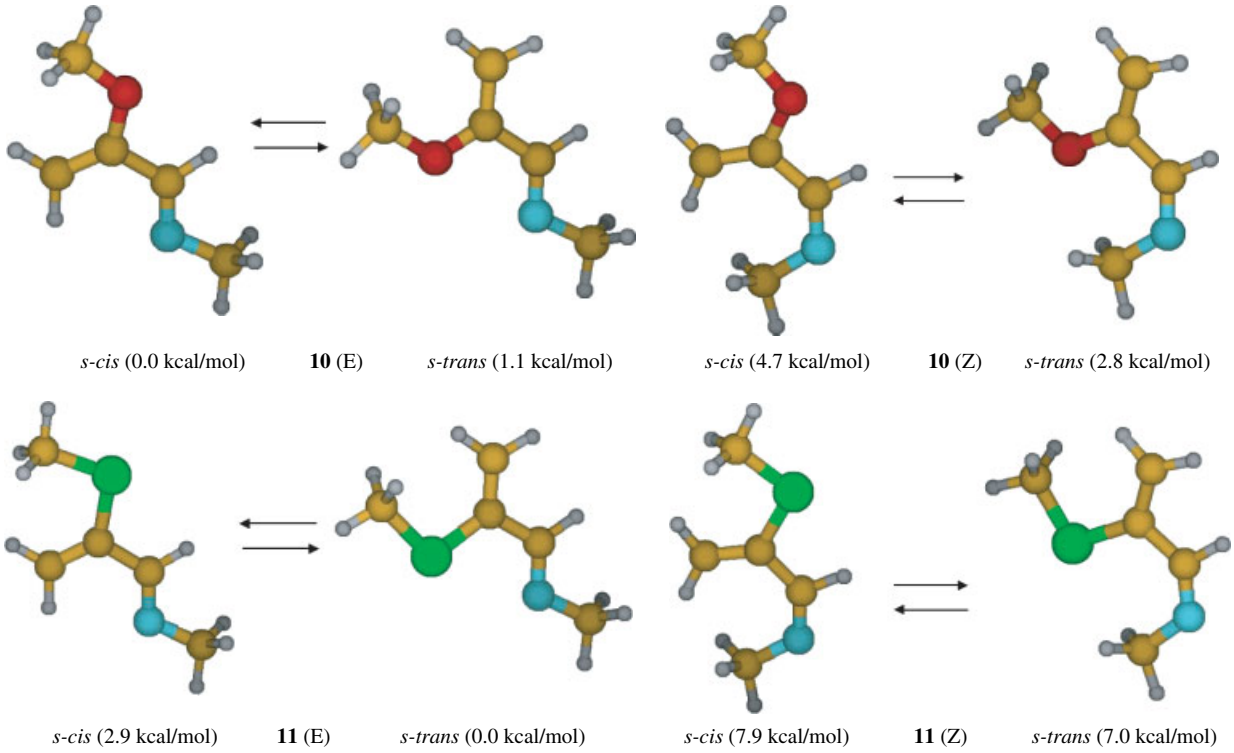


Figure 3. MP2/6–311G** optimized equilibrium conformations of *E* and *Z* isomers of the model azomethines (**10**) and (**11**). Relative energies are given in parentheses. Element colors: hydrogen – gray, carbon – yellow, oxygen – red, sulphur - green.

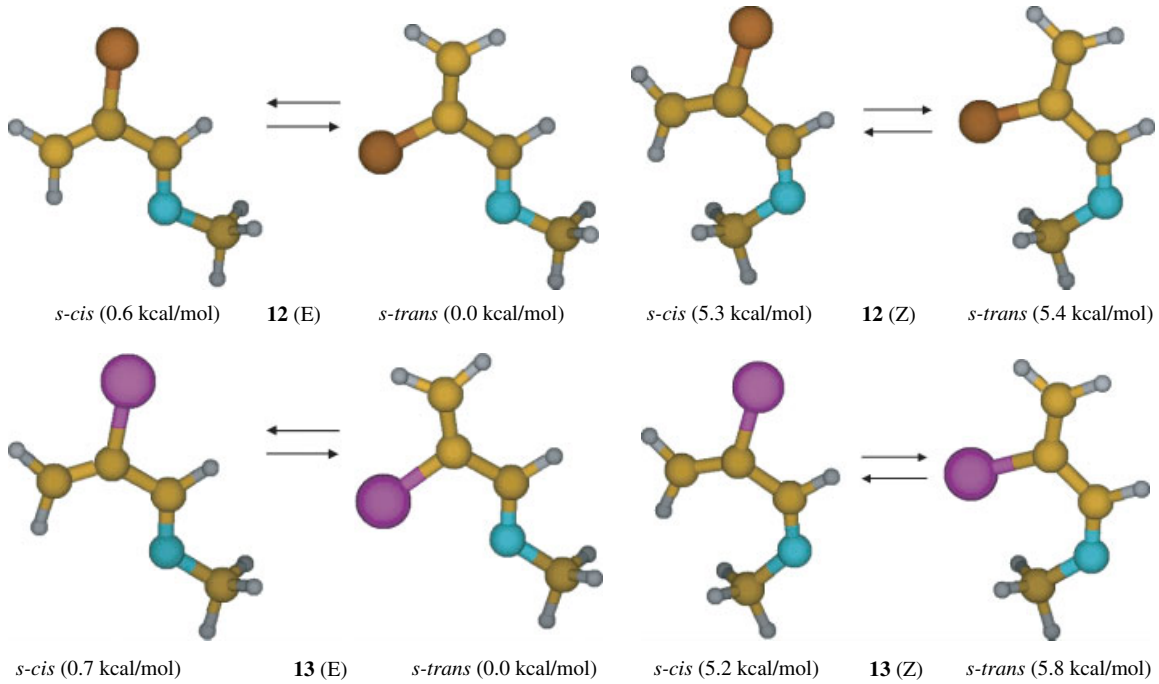
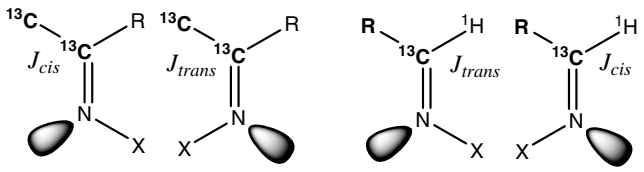


Figure 4. MP2/6–311G** optimized equilibrium conformations of *E* and *Z* isomers of the model azomethines (**12**) and (**13**). Relative energies are given in parentheses. Element colors: hydrogen – gray, carbon – yellow, chlorine – brown, bromine – violet.

values and provides an unambiguous guide to the configurational assignment at the C=N bond in a number of imino derivatives (RR′C=N–X, X = OH, OCH=CH_2, Alk, Ar, SO_2Ar).[6,7] The same is true for the one-bond ^1J(C,H) involving the α-imino carbon; however, this remarkable feature of ^1J(C,H) is much less known and is much less exploited in the stereochemical analysis. Apart from the main goal of the present study focusing on the configurational assignment of the synthesized azomethines **1–7**, another interesting aspect we dealt with was the potential applicability of the one-bond ^1J(C,H) involving the α-imino carbon used for the same purpose, i.e. for the configurational analysis of azomethines.

Calculations of ^1J(C,C) and ^1J(C,H) in the model series **8–13** were performed at the second-order polarization



propagator approach (SOPPA)[8] level approved for the calculation of spin–spin coupling constants of different types in a number of publications by Sauer *et al.*[9,10] Correlation-consistent basis set cc-pVDZ of Dunning *et al.*[11] augmented with the core *s*-functions of Woon and Dunning[12] on coupled carbons, cc-pVDZ-Cs, and basis set of Sauer *et al.*,[10f] aug-cc-pVTZ-J, with the tight *s*-functions of Schulman and Kaufman[13] on coupled hydrogens were applied, as described elsewhere.[14] It is noteworthy that augmenting the standard Dunning's correlation-consistent basis sets with either core or tight *s*-functions accounting for the correlation effects of inner electrons and improving the description of the cusp of the wavefunction at the position of the nucleus (which is crucial for the Fermi contact contribution) plays a key role in the accuracy of the SOPPA calculations of ^{1}J(C,C) and ^{1}J(C,H), as shown in a number of publications cited in the preceding text.[7,9,10,14]

Results of the SOPPA calculations of the title ^{1}J(C,C) and ^{1}J(C,H) in the model series **8–13** in comparison with the experimental values in the original compounds **1–7** are compiled in Table 2. First of all, it should be noted that both one-bond couplings involving the α-imino carbon, ^{1}J(C,C) and ^{1}J(C,H), show marked dependence on the orientation of the nitrogen lone pair in good agreement with the available experimental data which enables one to perform the unambiguous assignment of all of the parent azomethines **1–7** to the *E*-configuration. This is the main result of the present study.

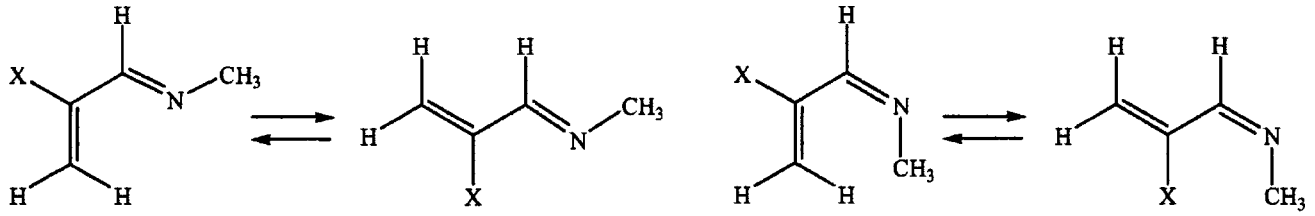
The marked difference of the calculated J_{cis} and J_{trans} for both types of couplings, ^{1}J(C,C) and ^{1}J(C,H), originating in the lone pair effect of the nitrogen atom of imino group is solely due to the changes in their Fermi contact contributions. The negative J_{PSO} and positive J_{DSO} and J_{SD} almost compensate each other, which makes the overall contribution of the noncontact terms next to negligible (Table 2).

It thus follows that the lone pair effect is the main factor governing the behavior of both couplings resulting in *ca* 15 Hz difference of ^{1}J(C,C) and *ca* 25 Hz difference of ^{1}J(C,H) in the diverse isomers of the title azomethines. This unique feature of ^{1}J(C,C) and ^{1}J(C,H) involving the α-imino carbon could be safely exploited for the unambiguous assignment of the individual isomers of azomethines; however, some minor factors are to be taken into account as well, namely, the substituent effects at the α- and β-positions of the C=C double bond and, on the other hand, the conformational dependence of the title couplings.

The α-substituent effect provides a well-known trend of increasing the one-bond ^{1}J(C, C) and ^{1}J(C,H) with the electronegativity of the substituent attached to one of the coupled nuclei together with the heavy atom effect. The β-substituent effect is shown in Table 3 for the different conformations of the *E*,*E* and *E*,*Z* isomers of the model azomethine derivative of α-dimethylamino propenal (**14**) optimized at the MP2/6–311G** level (Fig. 5), also showing the out-of-plane deviations on account of the reasons discussed in the preceding text. It is clearly seen that changing the position of the β-substituent (i.e. either in *cis* or in *trans* configuration to the azomethine moiety) does not provide any noticeable effect upon the values of either ^{1}J(C,C) or ^{1}J(C,H), and this is a very encouraging observation.

What is less encouraging in the present study, is a marked conformational behavior of both couplings, especially that of

Table 2. Spin–spin coupling constants ^{1}J(C,C) and ^{1}J(C,H) of the model azomethines **8–13** calculated at the SOPPA level[a]



Cmpd	X	Isomer	Coupled nuclei	Conformation	J_{DSO}	J_{PSO}	J_{SD}	J_{FC}	J	Experiment
8	H	*E*	C^1, C^α	*s-cis*	0.23	−1.53	1.31	65.88	65.89	63.3
				s-trans	0.23	−1.99	1.16	65.71	65.10	–
			C^1, H^α	*s-cis*	0.93	−0.25	0.28	154.10	155.06	156.1
				s-trans	0.97	−0.31	0.33	153.32	154.31	–
		Z	C^1, C^α	*s-cis*	0.23	−1.64	1.17	52.42	52.17	–
				s-trans	0.23	−1.82	1.17	52.21	51.80	–
			C^1, H^α	*s-cis*	0.87	−0.23	0.26	173.26	174.16	–
				s-trans	0.92	−0.33	0.29	173.53	174.41	–

(*continued overleaf*)

Table 2. (*Continued*)

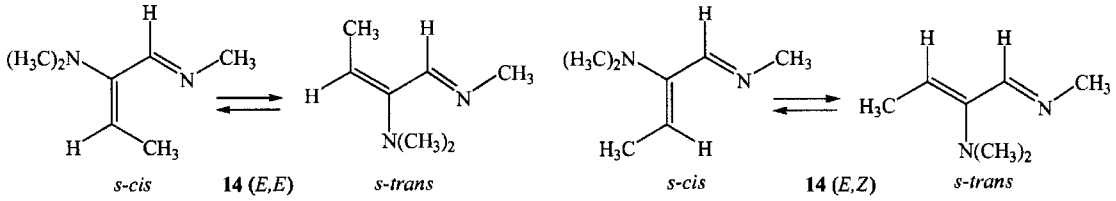
Cmpd	X	Isomer	Coupled nuclei	Conformation	J_{DSO}	J_{PSO}	J_{SD}	J_{FC}	J	Experiment
9	$N(CH_3)_2$	*E*	C^1, C^α	*s-cis*	0.32	−1.59	1.16	68.52	68.40	66.7
				s-trans	0.32	−1.78	0.89	66.80	66.22	–
			C^1, H^α	*s-cis*	1.13	−0.37	0.30	151.69	152.75	155.6
				s-trans	1.09	−0.41	0.36	156.84	157.87	–
		Z	C^1, C^α	*s-cis*	0.32	−1.40	0.70	53.78	53.40	–
				s-trans	0.32	−1.19	0.76	51.43	51.32	–
			C^1, H^α	*s-cis*	1.04	−0.42	0.32	177.45	178.39	–
				s-trans	1.01	−0.40	0.32	178.71	179.63	–
10	OCH_3	*E*	C^1, C^α	*s-cis*	0.31	−1.63	1.16	76.60	76.44	[b]
				s-trans	0.32	−1.79	1.01	73.32	72.85	–
			C^1, H^α	*s-cis*	1.07	−0.42	0.35	157.95	158.95	159.3
				s-trans	1.06	−0.32	0.34	155.56	156.65	–
		Z	C^1, C^α	*s-cis*	0.31	−1.75	1.01	59.61	59.17	–
				s-trans	0.32	−1.63	1.04	56.53	56.26	–
			C^1, H^α	*s-cis*	1.02	−0.40	0.34	181.28	182.24	–
				s-trans	1.00	−0.30	0.30	176.94	177.93	–
11	SCH_3	*E*	C^1, C^α	*s-cis*	0.31	−1.50	1.20	67.82	67.84	62.8
				s-trans	0.31	−1.85	1.00	65.33	64.79	–
			C^1, H^α	*s-cis*	1.09	−0.32	0.31	155.97	157.05	158.3
				s-trans	1.07	−0.37	0.36	157.13	158.19	–
		Z	C^1, C^α	*s-cis*	0.31	−1.62	1.04	51.39	51.12	–
				s-trans	0.31	−1.63	1.00	47.27	46.94	–
			C^1, H^α	*s-cis*	1.05	−0.27	0.28	177.36	178.41	–
				s-trans	1.01	−0.30	0.31	180.12	181.15	–
12	Cl	*E*	C^1, C^α	*s-cis*	0.31	−1.61	1.31	75.14	75.14	70.1
				s-trans	0.31	−1.93	1.08	72.32	71.79	–
			C^1, H^α	*s-cis*	1.07	−0.35	0.35	163.00	164.07	163.7
				s-trans	1.07	−0.29	0.35	157.08	158.20	–
		Z	C^1, C^α	*s-cis*	0.31	−1.76	1.15	54.11	53.80	–
				s-trans	0.31	−1.69	1.07	51.41	51.09	–
			C^1, H^α	*s-cis*	1.02	−0.30	0.33	186.75	187.80	–
				s-trans	1.01	−0.24	0.30	179.79	180.85	–
13	Br	*E*	C^1, C^α	*s-cis*	0.36	−1.65	1.32	76.42	76.45	69.3
				s-trans	0.37	−1.99	1.07	73.96	73.40	–
			C^1, H^α	*s-cis*	1.18	−0.35	0.37	165.98	167.19	167.4
				s-trans	1.13	−0.28	0.35	158.62	159.82	–
		Z	C^1, C^α	*s-cis*	0.36	−1.77	1.15	53.00	52.74	–
				s-trans	0.36	−1.74	1.03	50.11	49.76	–
			C^1, H^α	*s-cis*	1.14	−0.30	0.36	189.78	190.98	–
				s-trans	1.07	−0.23	0.30	181.61	182.76	–

[a] In the calculations of ^1J(C,C) and ^1J(C,H) the coupled carbons and coupled hydrogens were specified with the cc-pVDZ-Cs, and accordingly, with the aug-cc-pVTZ-J basis sets, while uncoupled carbons and hydrogens and the rest of the elements were assigned with cc-pVDZ with no polarization *p*-functions on hydrogens. The equilibrium MP2/6–311G** geometries were used throughout. All calculations were performed without symmetry constraints assuming the C_1 symmetry point group. All couplings and their contributions are in Hz.

[b] Not measured due to signal overlapping.

^1J(C,H), which can be traced out in the set of data of Table 2. Indeed, in the model azomethines bearing the heteroatomic α-substituents, namely, **10** (X = OCH_3), **12** (X = Cl) and **13** (X = Br), both couplings show very strong conformational dependence upon the orientation of the alkenyl moiety in respect to the C═N bond. In both isomers of **10**, **12** and **13** the values of $^1J(C^1, H^\alpha)$ are less by *ca* 6–8 Hz in the *s-trans* conformations, i.e. when the C^1–H^α and C^1–X bonds adopt the *s-trans* orientation. In our opinion, this marked conformational effect should be accounted for the charge transfer interaction $\sigma_{CH} - \sigma^*_{CX}$ (X = O, Cl and Br) involving electron density hyperconjugative transfer from the C–H bond to the

Table 3. Spin–spin coupling constants ^1J(C,C) and ^1J(C,H) of the model azomethine **14** calculated at the SOPPA level[a]



Isomer	Coupled nuclei	Conformation	J_{DSO}	J_{PSO}	J_{SD}	J_{FC}	J
14 (*E*,*E*)	C^1, C^α	*s-cis*	0.33	−1.74	0.75	70.68	70.01
		s-trans	0.33	−1.90	0.91	69.32	68.66
		s-cis	1.14	−0.49	0.34	155.39	156.38
	C^1, H^α	*s-trans*	1.15	−0.41	0.34	155.07	156.15
14 (*E*,*Z*)	C^1, C^α	*s-cis*	0.32	−1.67	0.89	70.71	70.25
		s-trans	0.32	−1.92	0.93	69.25	68.58
		s-cis	1.12	−0.51	0.34	155.87	156.82
	C^1, H^α	*s-trans*	1.11	−0.45	0.34	154.29	155.29

[a] See footnote to Table 2.

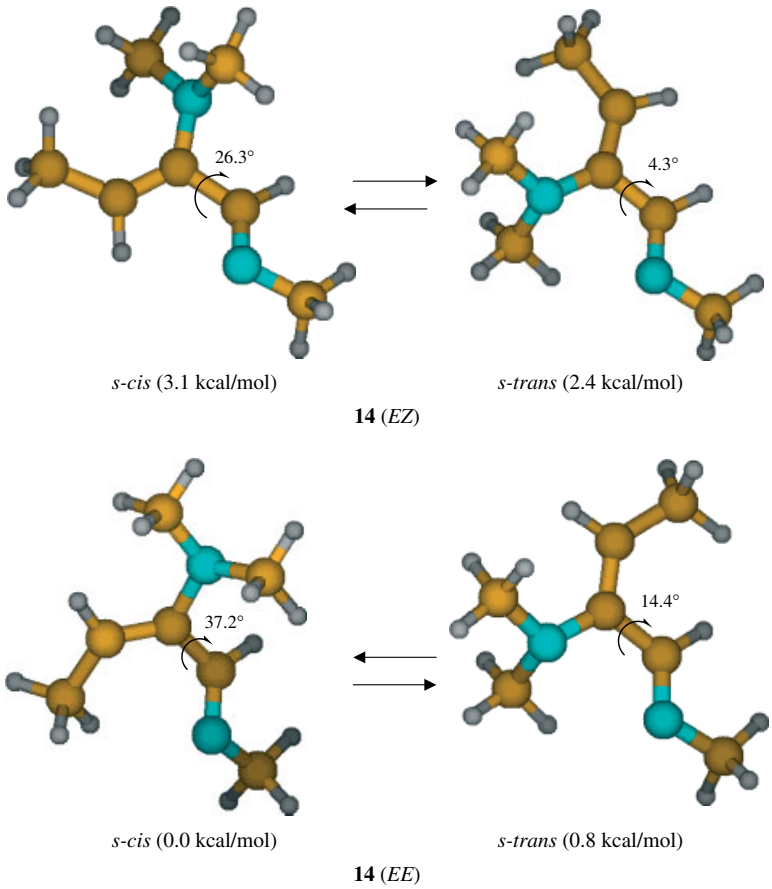


Figure 5. MP2/6–311G** optimized equilibrium conformations of *EE* and *EZ* isomers of the model azomethine (**14**); shown on the structures are the out-of-plane deviations. Relative energies are given in parentheses. Element colors: hydrogen – gray, carbon – yellow, nitrogen – cyan.

antibonding orbital of the C–X bond[15] which makes C–H bonds longer and weaker and, as a result, giving rise to smaller ^1J(C,H), (see reviews).[16] Fortunately, the overall conformational effect (*ca* 6–8 Hz) is much less than the lone pair effect (*ca* 25 Hz), which means that $^1J(C^1, H^\alpha)$ could be used safely for the configurational assignment of azomethines adopting different conformations. Conformational behavior of ^1J(C,C) is much less pronounced demonstrating the benefits of these couplings for the configurational studies of the conformationally nonhomogeneous imines.

Table 4. Specification of the basis sets used in the present SOPPA calculations of *J*(C,C) and *J*(C,H)

Atom(s)	Basis set	Number of basis AO (per atom)	Contraction[a]	Exponents of the core and/or tight *s*-functions	Contraction coefficient(s)
H-coupled	aug-cc-pVTZ-J	20	(10s, 3p, 1d) → [6s, 3p, 1d]	$\zeta_1 = 225.0$	0.0003665000
				$\zeta_2 = 1496.0$	0.0000425600
				$\zeta_3 = 9950.0$	0.0000030970
				$\zeta_4 = 66145.0$	0.0000004137
H-uncoupled	cc-VDZ[b]	2	(4s) → [2s]	[c]	[c]
C-coupled	cc-pVDZ-Cs	15	(10s, 4p, 1d) → [4s, 2p, 1d]	$\zeta_1 = 4.53$	1.0000000000
C-uncoupled	cc-pVDZ	14	(9s, 4p, 1d) → [3s, 2p, 1d]	[c]	[c]
N, O	cc-pVDZ	14	(9s, 4p, 1d) → [3s, 2p, 1d]	[c]	[c]
S, Cl	cc-pVDZ	18	(12s, 8p, 1d) → [4s, 3p, 1d]	[c]	[c]
Br	cc-pVDZ	27	(14s, 11p, 6d) → [5s, 4p, 2d]	[c]	[c]

[a] Spherical harmonic Gaussian functions (1s, 3p, 5d and 7f) are used; uncontracted core and/or tight *s*-functions are formally included into contraction schemes. Full sets of the contraction coefficients and exponents of the individual *s*-, *p*- and *d*-functions may be found in the original publications by Dunning *et al*.[11,12] and Sauer *et al*.[10f]

[b] Basis set cc-pVDZ without polarization *p*-functions, used for the uncoupled hydrogens only.

[c] Neither core nor tight *s*-functions are present in the contraction scheme.

CONCLUSIONS

Configurational assignment of the seven azomethine derivatives of the α-functionally substituted and nonsubstituted α,β-unsaturated aldehydes has been performed on the basis of the experimental measurements and SOPPA calculations of ^1J(C,C) and ^1J(C,H) involving the α-imino carbon expectedly demonstrating the marked orientational nitrogen lone pair effect. All the studied azomethines were established as the *E* isomers in respect to the configuration at the C=N bond, and no traces of the diverse *Z* isomer were observed in any circumstance.

A marked conformational behavior of ^1J(C,H) was established with respect to the orientation of the C=C and C=N double bonds, and this was attributed to the charge transfer interaction $\sigma_{CH} - \sigma^*_{CX}$ involving electron density hyperconjugative transfer from the C–H bond to the antibonding orbital of the C–X bond in the *s-trans* conformation. Fortunately, the overall conformational effect (*ca* 6–8 Hz) is much less than the lone pair effect (*ca* 25 Hz), which means that ^1J(C,H) could be used safely for the configurational assignment of the azomethines adopting different conformations. Conformational behavior of ^1J(C,C) is much less pronounced.

EXPERIMENTAL

NMR measurements

^{13}C NMR spectra were recorded on a Bruker AVANCE 400 MHz spectrometer in a 10-mm broadband probe at 300 K (solvents specified in the following text) with HMDS as an internal standard. Carbon–carbon coupling constants were measured using the INADEQUATE pulse sequence of Bax, Freeman and Kempsell[17] adjusted for $J = 70$ Hz. Settings for the INADEQUATE experiments were as follows: 90° pulse length, 12–14 μs; spectral width, 10–15 kHz; acquisition time, 4–6 s; relaxation delay, 6–10 s; characteristic delay $\tau = 1/4J$, 3.6 ms; digital resolution 0.05–0.1 Hz/pt.

Computational details

Geometric optimizations were performed with the GAMESS code[18] at the MP2 level[19] using the 6–311G** basis set of Pople and coworkers,[20] without symmetry constraints assuming the C_1 symmetry point group. Calculations of spin–spin coupling constants have been carried out using the DALTON package[21] at the SOPPA level[8] with the correlation-consistent basis sets of Dunning and coworkers[11,12] and Sauer *et al*.,[10f] either taken from the Dalton Basis Sets Library[21] as they stand or slightly modified by adding or removing polarization, core, tight or diffuse functions, as specified in Table 4. The SOPPA calculations of ^1J(C,C) and ^1J(C,H) were performed within the C_1 point group, and all compounds were adopted in their equilibrium conformations located at the MP2/6–311G** level.

Synthesis of 1–7

2-[(3-Phenyl-2-propenylidene)amino]-1-ethanol (**1**) was prepared according to Ref. 22 starting from 3-phenyl-2-propenal and 2-aminoethanol. ^{1}H chemical shifts, $CDCl_3$ (δ, ppm): 3.60–3.65 (m, 2H, NCH_2); 3.80–3.90 (m, 2H, OCH_2); 4.27 (br.s., 1H, OH); 6.83–6.90 (m, 2H, 2CH=); 7.30–7.45 (m, 5H, Ph); 8.00 (d, $J = 7.0$, 1H, CH=N); ^{13}C chemical shifts, $CDCl_3$ (δ, ppm): 61.98 (NCH_2); 63.32 (OCH_2); 135.54 (C^i.); 128.79 (C^o.); 127.29 (C^m.); 127.50 (C^p.); 129.28 (CH=); 142.40 (Ph-CH=); 164.77 (CH=N).

2-Methyl-2-[(3-phenyl-2-propenylidene)amino]-1-propanol (**2**) was prepared according to the similar procedure starting from 3-phenyl-2-propenal and 2-amino-2-methyl-1-propanol. ^{1}H chemical shifts, DMFA (δ, ppm): 1.16 (s, 6H, CH_3); 2.52 (br.s., 1H, OH); 3.39 (s, 2H, CH_2); 6.87 (dd, $J = 16.1$, 8.6, 1H, CH=); 7.08 (d, $J = 16.1$, 1H, Ph-CH=); 7.33–7.43 (m, 3H, Ph); 7.52–7.60 (m, 2H, Ph); 8.12 (d, $J = 8.6$, 1H, CH=N); ^{13}C chemical shifts, DMFA (δ, ppm): 24.20 (Me); 61.63 (CMe_2); 70.71 (CH_2O); 136.71 (C^i.); 129.33 (C^o.); 127.62 (C^m.); 129.34 (C^p.); 130.05 (CH=); 141.13 (Ph-CH=); 159.15 (CH=N).

MRC

*N-(2-piperidino-2-butenylidene)methanamine (**3**)* was prepared as a mixture (1 : 1.5) of *EZ*- and *EE*-isomers by the reaction of 2-piperidino-2-butenal with methylamine hydrochloride at the present of K_2CO_3, as described elsewhere.[23] ^{1}H chemical shifts, $CDCl_3$ (δ, ppm): *EZ*-isomer: 1.45–1.60 (m, 6H, $(CH_2)_3$); 1.91 (d, J = 7.3, 3H, CH_3); 2.60–2.75 (m, 4H, $N(CH_2)_2$); 3.31 (d, J = 1.4, 3H, NMe); 5.47 (q, J = 7.3, 1H, CH═); 7.69 (q, J = 1.4, 1H, CH═N); *EE*-isomer: 1.45–1.60 (m, 6H, $(CH_2)_3$); 1.87 (d, J = 7.3, 3H, CH_3); 2.60–2.75 (m, 4H, $N(CH_2)_2$); 3.43 (d, J = 1.7, 3H, NMe); 5.08 (q, J = 7.3, 1H, CH═); 8.05 (q, J = 1.7, 1H, CH═N); ^{13}C chemical shifts, $CDCl_3$ (δ, ppm): *EZ*-isomer: 12.98 (CH_3); 51.33 (C^{α} piperidine); 26.67 (C^{β} piperidine); 24.25 (C^{γ} piperidine); 47.91 (NMe); 124.96 (CH═); 148.50 (═C–N); 163.03 (C═N); *EE*-isomer: 12.31 (CH_3); 51.33 (C^{α} piperidine); 25.76 (C^{β} piperidine); 24.28 (C^{γ} piperidine); 48.37 (NMe); 111.44 (CH═); 147.80 (═C–N); 158.60 (C═N).

*N-(2-ethoxy-2-propenylidene)butanamine (**4**)* was synthesized as reported earlier.[24] ^{1}H chemical shifts, $CDCl_3$ (δ, ppm): 0.54 (t, J = 7.5, 3H, CH_3); 0.90–1.00 (m, 2H, CH_2); 1.05 (t, J = 7.0, 3H, CH_3); 1.20–1.30 (m, 2H, CH_2); 3.13 (t, J = 7.0, 2H, NCH_2); 3.50 (q, J = 7.0, 2H, OCH_2); 4.18 (d, J = 10.8, CH_2═); 7.28 (s, 1H, CH═N); ^{13}C chemical shifts, $CDCl_3$ (δ, ppm): 12.84 (CH_3 *n*-Bu); 13.24 (CH_3); 60.22 (C^{α} *n*-Bu); 31.74 (C^{β} *n*-Bu); 19.43 (C^{γ} *n*-Bu); 62.42 (OCH_2); 92.30 (CH_2═); 156.71 (═C–O); 156.75 (C═N).

*N-[2-(butylsulfanyl)-3-phenyl-2-propenylidene]methanamine (**5**)* was prepared as follows: 2-Butylsulfanyl-3-phenyl-2-propenal (1.5 g, 6.8 mmol) was added to methylamine hydrochloride (3.5 g, 52 mmol) in benzene at room temperature (rt). The reaction mixture left out for 24 h. After filtration solvent was removed under reduced pressure, the residue was distilled as a mixture of *EZ* and *EE* isomers. ^{1}H chemical shifts, $CDCl_3$ (δ, ppm): *EZ*-isomer: 0.77 (t, J = 7.4, 3H, CH_3); 1.20–1.30 (m, 2H, CH_2); 1.40–1.50 (m, 2H, CH_2); 2.80 (t, J = 7.4, 3H, CH_3); 3.46 (s, 3H, NMe); 7.13 (s, 1H, CH═); 7.15–7.40 (m, 3H, arom.); 7.70–7.80 (m, 2H, arom.); 7.95 (s, 1H, CH═N); *EE*-isomer: 0.91 (t, J = 7.4, 3H, CH_3); 1.40–1.50 (m, 2H, CH_2); 1.63–1.73 (m, 2H, CH_2); 2.80 (t, J = 7.4, 3H, CH_3); 3.40 (s, 3H, NMe); 6.83 (s, 1H, CH═); 7.15–7.40 (m, 3H, arom.); 7.70–7.80 (m, 2H, arom.); 8.22 (s, 1H, CH═N); ^{13}C chemical shifts, $CDCl_3$ (δ, ppm): *EZ*-isomer: 13.58 (CH_3); 21.82, 30.25, 32.70 (CH_2); 47.92 (NMe); 135.65 (C^{i}.); 130.35 (C^{o}.); 128.13 (C^{m}.); 127.52 (C^{p}.); 131.01 (CH═); 134.07 (═C–S), 164.11 (C═N); *EE*-isomer: 13.71 (CH_3); 22.25, 30.72, 31.78 (CH_2); 48.05 (NMe); 136.09 (C^{i}.); 129.30 (C^{o}.); 128.37 (C^{m}.); 128.58 (C^{p}.); 131.26 (CH═); 137.28 (═C–S); 159.63 (C═N).

*N-(2-chloro-3,3-diphenyl-2-propenylidene)-N-cyclohexylamine (**6**)* was prepared starting from 2-chloro-3,3-diphenylpropenal and trimethylsilylcyclohexylamine according to the reported procedure.[25] ^{1}H chemical shifts, $CDCl_3$ (δ, ppm): 1.20–1.30 (m, 2H); 1.55–1.70 (m, 8H); 3.00–3.10 (m, 1H); 7.20–7.40 (m, 10H); 8.02 (s, 1H); ^{13}C chemical shifts, $CDCl_3$ (δ, ppm): 69.47 (C^{α} cyclohexyl); 34.07 (C^{β} cyclohexyl); 24.82 (C^{γ} cyclohexyl); 25.49(C^{δ} cyclohexyl); 139.33, 140.46 (C^{i}); 129.64, 130.42(C^{o}); 128.05, 128.35(C^{m}); 128.27, 128.54(C^{p}); 129.92 (═CCl); 148.76 (Ph_2C═); 155.10 (CH═N).

*N-(2-bromo-3-phenyl-2-propenylidene)-N-(trimethylsilyl) amine (**7**)* was prepared by the reaction of 2-bromo-3-phenyl-2-propenal with hexamethyldisilazane according to Ref. 26 ^{1}H chemical shifts, $CDCl_3$ (δ, ppm): 0.24 (s, 9H, $SiMe_3$); 7.25–7.45 (m, 3H, arom.); 7.54 (s, 1H, CH═); 7.85–7.90 (m, 2H, arom.); 8.22 (s, 1H, CH═N); ^{13}C chemical shifts, $CDCl_3$ (δ, ppm): 1.91 ($SiMe_3$); 122.69 (═C–Br); 129.36, 129.77, 130.25, 134.52 (C arom.); 141.51 (CH═); 158.68 (CH═N).

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