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Investigation of the configuration of alkyl phenyl ketone phenylhydrazones from *ab initio* ^{1}H NMR chemical shifts†

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Using *ab initio* GIAO calculations the experimental ^{1}H NMR spectra of the *E* and *Z* isomers of alkyl phenyl ketone phenylhydrazones R1–C(Ph)=N–NH–Ph (R1 = Me, Et, iPr, and tBu) have been re-interpreted and deviations from Karabatsos' rule or from the assignment of Bellamy and Hunter have been discussed in the light of the optimized geometrical structures.

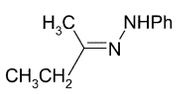
I Introduction

Compounds containing the sequence X–C=N–Y generally exist under the form of a mixture of two isomers, *syn* and *anti*, and are also referred to as *Z* and *E*. Several works concerning the isomerization equilibria of imines (X = R, Y = R′),[1] oximes (X = R, Y = OH),[2] iminoesters (X = OR, Y = R′),[3] hydrazones (X = R, Y = NR′R″)[4] and hydroximates (X = OR, Y = OH)[5] are known. The hydrazonates (X = OR, Y = NR′R″)[6] have however been much less studied. Recently, we initiated a study of the conformation of a series of hydrazonates with various substituents,[7,8] in which we aimed at combining experimental ^{1}H NMR spectroscopic determinations with *ab initio* quantum chemical calculations. Indeed, it has been shown that NMR is a convenient and accurate method for assigning the *syn* and *anti* structures of, for instance, hydrazone isomers[9] and theory can help in interpreting the results. Due to the structural similarities of the hydrazonates and hydrazones, the characterization of the hydrazonate conformations has been based on the structure–NMR relationships of related hydrazones.[6] Therefore, further understanding of the relationship between the conformations of hydrazones and their ^{1}H NMR spectra should provide useful information in regard our initial purpose and it is the subject of the present investigation.

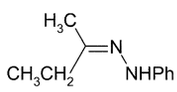
Both in solution and in the pure state, hydrazones derived from ketones are present as mixtures of two configurations in equilibrium (Scheme 1).

Scheme 1

In their previous works employing the ^{1}H NMR technique, Karabatsos and co-workers[4,9] observed that for hydrazones derived from phenylhydrazine (R = H, R′ = Ph), the signal associated with the hydrocarbon substituents attached to the hydrazonic carbon appears at high fields when the group is in *syn* position with respect to NH–Ph and at low fields when it is in *anti*. This will be referred to as the Karabatsos' rule.[4] For instance, for the compound with R1 = Me and R2 = Et in CCl_4,[9] the ^{1}H NMR chemical shifts of the R1 and R2 groups, *i.e.* of the protons in positions α and β to the C=N group, are described in Scheme 2



E



Z

	E	Z
CH$_3$ (α) (ppm)	1.60 (syn)	1.88 (anti)
CH$_2$ (α) (ppm)	2.22 (anti)	2.03 (syn)
CH$_3$ (β) (ppm)	1.07 (anti)	0.97 (syn)

Scheme 2

However, Bellamy and Hunter[10] found later that this rule provides incorrect assignments with sterically-hindered alkyl phenyl ketone phenylhydrazones (R = H, R′ = Ph, R1 = alkyl, R2 = Ph). Their reasoning was based on UV spectra while the anomalies in the ^{1}H NMR spectra were explained in terms of the loss of co-planarity between the phenyl group (R2) and the C=N plane that induces motion of the alkyl group from the deshielding to the shielding region of the phenyl (R2) group. This was based on the assumption that the dihedral angle between the Ph group and the C=N plane will be larger for the *Z* than for the *E* conformer so that Karabatsos'rule could be reversed.

The present work aims i) at characterizing the structural properties of these alkyl phenyl hydrazones by applying *ab initio* methods, ii) at deducing, from calculations of the *ab initio* Gauge-Invariant Atomic Orbital (GIAO)[11] nuclear shielding constants, the relationship between conformation and ^{1}H NMR spectra, and iii) at assessing Karabatsos'rule and its exceptions pointed out by Bellamy and Hunter. Previous theoretical investigations have addressed conformational effects in hydrazones, either by investigating *ab initio* the conformational transition of model systems[12] or by studying with semi-empirical methods the R = Ph ring substitution effects on the relative stability of the *E* and *Z* isomers.[13] Nevertheless, to our knowledge, ^{1}H NMR chemical shifts have not been considered. Section II describes and substantiates the computational approach while the results are presented and analyzed in Section III before we conclude in Section IV.

II Computational procedure

The geometry optimizations were carried out using the hybrid B3LYP exchange-correlation (XC) functional[14] and the 6-31G(d) basis set.[15] Recent works have reminded us that this basis set is necessary for geometry optimization of polar bonds

† Electronic supplementary information (ESI) available: Full geometry optimization at the B3LYP/6-31G(d) level of approximation. See http://www.rsc.org/suppdata/ob/b3/b307528a/

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Table 1 Basis set effects on the ^{1}H chemical shifts (in ppm) of the *Z* and *E* conformers of Et–C(Me)=N–NH–Ph. The geometries have been optimized at the B3LYP/6-31G(d) level of approximation and the *syn*/*anti* notation refers to the relative position with respect to the NH–Ph group. *Δ* is the difference of chemical shift between the *anti* and *syn* positions

	δ		
Basis set	*E*	*Z*	Δ
CH_3 (α)	*syn*	*anti*	
6-31G(d)	1.61	1.94	0.33
6-311+G(2d,p)	1.78	2.03	0.25
6-311++G(d,p)	1.79	2.06	0.27
6-311++G(2d,p)	1.78	2.02	0.24
Experiment[a]	**1.60** ± **0.03**	**1.88** ± **0.03**	**0.28** ± **0.006**
6-311+G(2d,p) with scaling (0.95)	1.69	1.92	0.23
CH_2 (α)	*anti*	*syn*	
6-31G(d)	2.44	2.11	0.33
6-311+G(2d,p)	2.41	2.21	0.20
6-311++G(d,p)	2.45	2.22	0.23
6-311++G(2d,p)	2.42	2.23	0.19
Experiment[a]	**2.22** ± **0.03**	**2.03** ± **0.03**	**0.19** ± **0.006**
6-311+G(2d,p) with scaling (0.95)	2.29	2.11	0.18
CH_3 (β)	*anti*	*syn*	
6-31G(d)	1.19	1.09	0.10
6-311+G(2d,p)	1.20	1.07	0.13
6-311++G(d,p)	1.26	1.14	0.12
6-311++G(2d,p)	1.21	1.08	0.13
Experiment[a]	**1.07** ± **0.03**	**0.97** ± **0.03**	**0.10** ± **0.006**
6-311+G(2d,p) with scaling (0.95)	1.14	1.02	0.12

[a] Ref. 9, values obtained in CCl_4 solution.

whereas more extended basis sets do not provide any significant improvement.[16] The B3LYP approach is characterized by a weighted combination of the local VWN[17] and nonlocal LYP[18] functionals for the correlation part and by a mixture of three functionals for defining the exchange, *i.e.* the local Slater exchange,[19] the Hartree–Fock exchange and Becke's[20] functional which describes the density gradient corrections to the Slater exchange. This method has been used to compare the relative stability of the *Z* and *E* isomers. For some isomerization equilibria, zero-point vibrational energy (ZPE) as well as thermal corrections ($T = 298.15$ K) have been included in order to estimate the differences in free enthalpy between the various isomers (ΔG^{298}_0). All these calculations as well as the evaluation of the NMR shielding constants have been performed by using the Gaussian 98 program.[21]

The theoretical NMR chemical shifts were calculated as the differences in isotropic shielding constants with respect to the reference (tetramethylsilane, TMS) molecule. To evaluate the shielding tensors, the GIAO[11] method was employed at the B3LYP level of approximation with several basis sets. This approach based on density functional theory (DFT) has turned out to be a good compromise between computational cost and reliability because most of the error in the proton magnetic shielding calculations is systematic in nature and can therefore be corrected by a linear scaling procedure.[22] Indeed, Table 1 shows that in the case of Et–C(Me)=N–NH–Ph the basis set effects on the chemical shifts are small provided the basis set contains polarization and diffuse functions.

From these results, we selected the 6-311+G(2d,p) basis set and, following Rablen *et al.*[23]—although in a slightly different way—have further improved the chemical shift estimates by multiplying them by a scaling factor of 0.95. This factor of 0.95 originates from averaging the slopes between the experimental chemical shifts and the calculated shielding constants obtained at similar levels of approximation.[23] This factor accounts i) for solvent—assumed in ref. 21 to be CCl_4 or $CDCl_3$—effects that, alternatively, can be taken into account, for instance, by using the polarizable continuum model approach of Cammi *et al.*,[24] ii) for missing electron correlation effects,[25] iii) for the finite size of the basis set, iv) for rovibrational contributions[26] as well as for temperature effects.[27] With this approach, the estimated chemical shifts are within the predicted error bars of ±0.15 ppm.[23] Indeed, in the case of the hydrazone of Table 1, theory systematically overestimates *δ* by 0.06 ± 0.03 ppm. When considering the difference in chemical shifts between the *anti* and *syn* conformers, $\Delta = \delta_{anti} - \delta_{syn}$, a better accuracy is reached and amounts, in the present case, to 0.03 ± 0.02 ppm. Although the data obtained with different basis sets are not detailed for other hydrazones, results presented in Section III further support the selection of the B3LYP/6-311+G(2d,p) method for ^{1}H NMR shielding constant determination.

III Results and discussion

Table 2 reports the calculated chemical shifts of the protons in positions α and β to the C=N group in comparison with the assignments of the recorded values by Bellamy and Hunter[10] as well as the composition of the *E* and *Z* isomers. Bellamy and Hunter[10] concluded that for R1 = Me the most abundant isomer is *E* whereas for R1 = iPr and R1 = tBu, it is *Z* as a result of the increased steric repulsions between the hydrazonic substituents. When R1 = Et, the *E* : *Z* ratio is very close to unity (51 : 49). The theoretical B3LYP/6-311+G(2d,p) energies (corresponding to internal energies at 0 K) are in qualitative agreement with ref. 10, *i.e.* the relative stability of the *Z* isomer with respect to the *E* isomer increases with the size of the substituent R1. However, if considering the R1 = Et compound for which the *E* : *Z* composition in CCl_4 solution is 49 : 51, it turns out that theory underestimates the relative stability of the *Z* isomer by about 0.7 kcal mol^{-1}. A similar conclusion can be drawn by comparing the *E* : *Z* composition and Δ*E*(B3LYP/6-311+G(2d,p)) values for R1 = Me and iPr because the Δ*E* value

Table 2 Chemical shifts (in ppm) for H_α and H_β of the hydrazonic carbon in the *Z* and *E* conformers of R1–C(Ph)=N–NH–Ph calculated at the B3LYP/6-311+G(2d,p) level of approximation with a scaling factor of 0.95

			δ			
			E (R1 in *syn* wrt NH–Ph)		*Z* (R1 in *anti* wrt NH–Ph)	
R1		*E* : *Z* composition [a]	H_α	H_β	H_α	H_β
Me	Th.	−1.6	2.04	—	2.19	—
	Exp.[b]	96 : 4	2.18	—	2.26	—
Et	Th.	−0.7	2.54	1.19	2.66	0.86
	Exp.[b]	49 : 51	2.19	0.84	2.56	1.18
	Exp Corr[c]		2.19	1.18	2.56	0.84
iPr	Th.	4.1	3.23	1.34	2.79	1.08
	Exp.[b]	18 : 82	3.14	1.30	2.77	1.13
tBu	Th.	7.6	—	1.21	—	1.13
	Exp.[b]	1 : 99	—	1.27	—	1.20

[a] The *E* : *Z* composition is theoretically characterized by B3LYP/6-311+G(2d,p) $\Delta E = E(E) - E(Z)$ values (in kcal mol^{-1}), whereas percentage compositions are provided for the experimentally derived values. [b] Ref. 10 (R1 = Me, iPr, and tBu in CCl_4; R1 = Et in benzene). [c] Proposed correction of the experimental assignment.

is expected to be larger for R1 = Me than for R1 = iPr. These inaccuracies can be attributed to the omission of solvent effects from the treatment and to the limitations of the method. For R1 = Et, the ZPE and thermal corrections (T = 298.15K) amount to 0.2 kcal mol^{-1} and an improved value of ΔG_0^{298} = −0.5 kcal mol^{-1} results. Since a first approximation to the electrostatic stabilization of a solute molecule is proportional to the square of the dipole moment, solvent effects can be qualitatively estimated by comparing the isomer dipole moments. Although this is a crude approximation which lacks consideration of geometry relaxation and higher-order multipole effects,[28] it accounts for some of the difference between theory and experiment because the dipole moment is larger for the *Z* isomer than for the *E* isomer [for R1 = Me, Et, iPr, and tBu, the dipole moments of the *E* isomers are 2.25, 2.31, 2.48, and 2.47 D, respectively, whereas for the *Z* isomer, given in the same order, the values are 2.94, 2.94, 2.92, and 2.84 D]. Indeed, by using the expression of the energy of a dipole in its own reaction field[29] to approximate the solvation energy (ε_{CCl_4} = 2.23), ΔE becomes −1.1 kcal mol^{-1}, −0.2 kcal mol^{-1}, 4.5 kcal mol^{-1}, and 7.9 kcal mol^{-1} for R1 = Me, Et, iPr, and tBu, respectively. This improves the agreement with the experimental *E* : *Z* compositions for R1 = Et whereas it is detrimental for R1 = Me and R1 = iPr. Although further refinement of our theoretical estimates is beyond the scope of this paper, it is nevertheless interesting to point out that the empirical substituent parameters of Knorr[30] for predicting the *E*–*Z* equilibrium constants reproduce to a large extent the *ab initio* results of ΔE and their limitations. Indeed, this model, which assumes that steric interactions are predominant, predicts the *E* isomer to be more abundant (74%) for R1 = Et and the *Z* isomer proportion to amount to 99% for the R1 = iPr compound. Predictions for R1 = Me and R1 = tBu are in better agreement with experiment.

For R1 = Me, Karabatsos' rule is verified both with the theoretical calculations and with the assignments given in ref. 10, *i.e.* $\delta(H_\alpha)$ is smaller when the NH–Ph group is in the *syn* position with respect to R1 (*E* isomer). For R1 = iPr and tBu, theory supports the hypothesis of ref. 10 which deviates from Karabatsos'rule. In the case of R1 = Et in the *syn* position, theory predicts stronger shielding of the protons in the α position (in agreement with Karabatsos'rule) but also stronger deshielding for the protons in the β position (in disagreement with Karabatsos' rule). The experimental assignment[10] leads to the same conclusion for the hydrogens in the α position but not for those in the β position. Since the *E* and *Z* isomers of the R1 = Et compound are in almost equal proportions, error in the experimental assignment is not to be excluded and we make the hypothesis that the correct experimental assignments for the H_α/H_β chemical shifts is 2.19/1.18 ppm and 2.56/0.84 ppm for the *E* and *Z* conformers, respectively. Although qualitative agreement is met, there remains a large difference between theory and experimental values for the CH_2 group when in the *syn* position with respect to the NH–Ph group.

In order to understand the chemical shift variations, the differences in the most significant geometrical parameters between *E* and *Z* isomers on changing the substituents were analyzed (Table 3). The C=N and N–N bond lengths are sensitive to the substituents as well as to the conformation whereas the N–C bond length changes by less than 0.002 Å, with the exception of R1 = tBu. For all compounds, the R = Ph ring and the C=N–NH group are coplanar (Fig. 1). The situation is different for the other Ph (= R2) ring. When the latter is coplanar—or almost coplanar—to the C=N–N group, electronic delocalization occurs and the C=N (N–N) bond length increases (decreases) by 0.010 (0.014) Å. These values have been determined from comparison between, on the one hand, the *E* isomer of (R1, R2) = (Et, Ph) and, on the other hand, the (R1, R2) = (Et, Me) compound in which π-conjugation is absent. In the *E* isomer, coplanarity is almost attained for R1 = Et (θ = 165.0°) and decreases in R1 = Me (θ = 158.8°), R1 = iPr (θ = 151.5°), and R1 = tBu (θ = 117.7°). In the case of the *Z* isomers, as a result of the steric repulsion with the NH group, the torsion with respect to the *E* isomers increases by 30–40° and the π-delocalization is reduced. The similarity between the θ values for R1 = Me, Et, and iPr rules out part of the explanation of Bellamy and Hunter[10] which is based on a larger departure from planarity of the phenyl ring in R1 = iPr than in R1 = Me when going from *E* to *Z*. On the other hand, the orientation of the R2 = Ph group affects the position of the R1 substituent as shown in the last column of Table 3 and in Fig. 1. For R1 = iPr in the *E* conformation, the H_α points towards the NH group whereas in the *Z* conformation, it is oriented in the direction of the R2 = Ph ring and undergoes a positive shielding due to this Ph ring. Such an effect is absent for R1 = Me because the signal is an average over the three H_α chemical shifts. Like the H_α of R1 = iPr, in the case of the H_β of the R1 = iPr and tBu compounds, the larger shielding of the *Z* conformer is related to the orientation of the R2 = Ph group and its positive cone. The very large shielding characterizing the H_β of the R1 = Et compound in the *Z* conformation has a similar origin: the positive shielding cone of the R2 = Ph ring. In the corresponding *E* conformer, the distance between R2 and

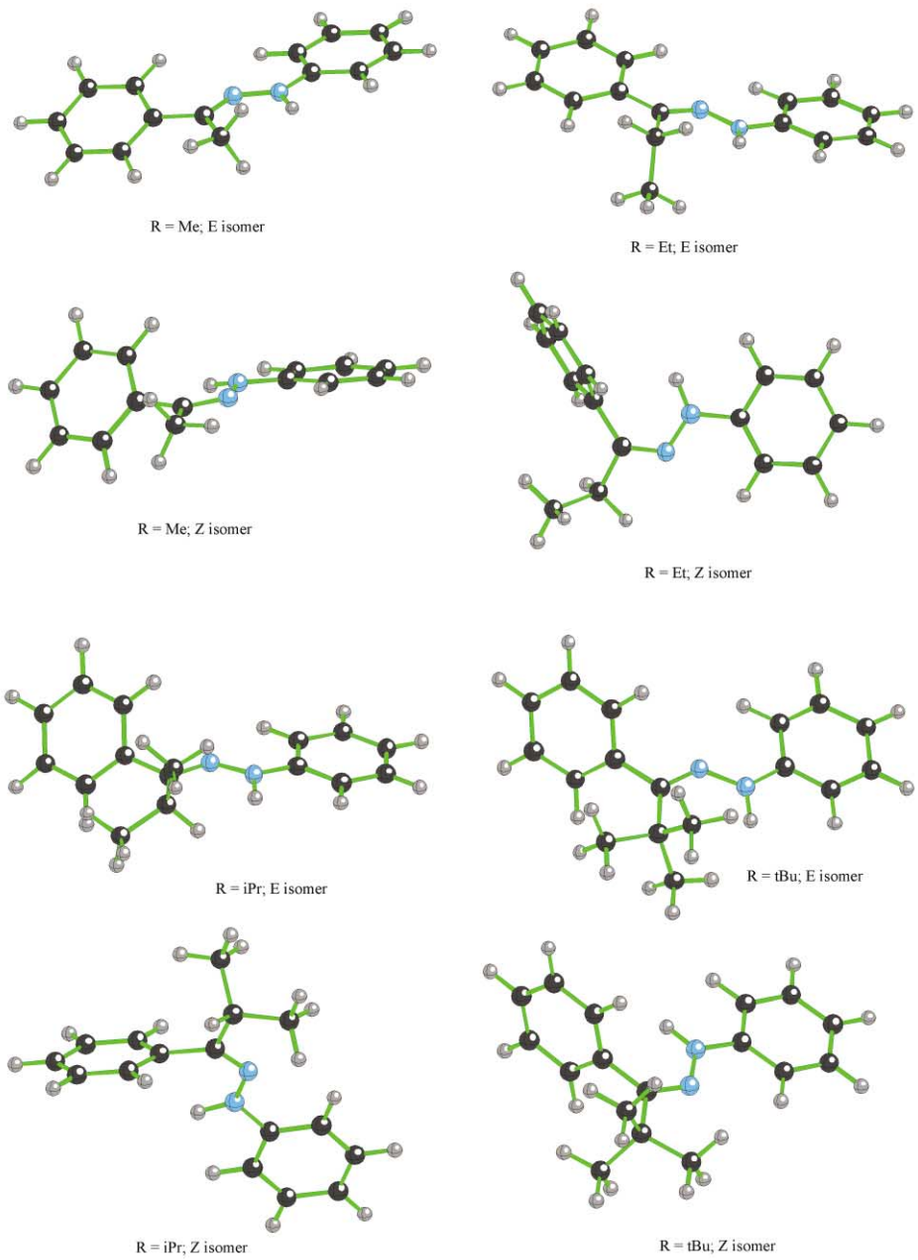

Fig. 1 Sketch of the B3LYP/6-31G(d)-optimized *E* and *Z* isomers of R–C(Ph)=N–NH–Ph.

Table 3 Key geometrical parameters of the *E* and *Z* isomers of R1–C(R2)=N–NH–Ph optimized at the B3LYP/6-31G(d) level of approximation

R1/R2	Isomer	$d_{C=N}$/Å	d_{N-N}/Å	$d_{N-C(Ph)}$/Å	$\theta_{NCC\alpha(Ph)C\beta(Ph)}$/°	$\theta_{NCC\alpha(R1)C\beta(R1)}$/°
Me/Et	*E*	1.287	1.358	1.396	—	0.2
	Z	1.288	1.359	1.398	—	80.3
Me/Ph	*E*	1.297	1.345	1.396	158.8	—
	Z	1.292	1.353	1.397	128.3	—
Et/Ph	*E*	1.297	1.344	1.396	165.0	82.5
	Z	1.293	1.353	1.397	126.4	114.2
iPr/Ph	*E*	1.296	1.344	1.396	151.5	—
	Z	1.291	1.352	1.396	122.1	—
tBu/Ph	*E*	1.294	1.348	1.400	117.7	—
	Z	1.291	1.349	1.393	88.5	—

the terminal CH_3 group is larger and δ is larger. This accounts for the modification of the assignment by Bellamy and Hunter.[10] The situation of the H_α atoms in R1 = Et is more complex and is considered in the next paragraph.

The influence of the R2 = Ph group orientation on the chemical shifts was further investigated by scanning the torsion angle from 0 to 180° for R1 = Et. For each value of θ, the remaining geometrical degrees of freedom were frozen at their

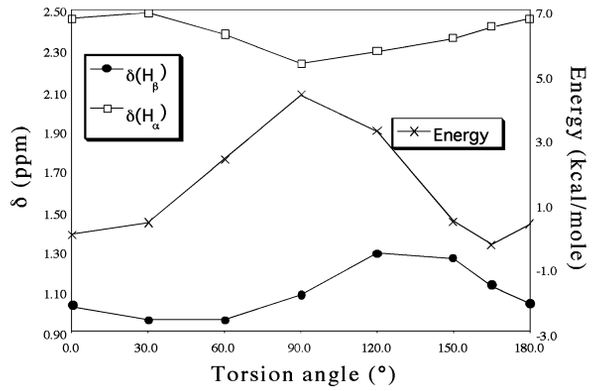

Fig. 2 Variations of the H_α and H_β chemical shifts in the *E* isomer of Et–C(Ph)=N–NH–Ph as a function of the R2 = Ph torsion angle and in comparison with the total energy.

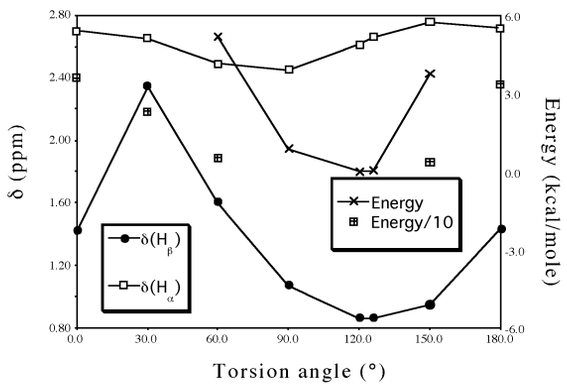

Fig. 3 Variations of the H_α and H_β chemical shifts in the *Z* isomer of Et–C(Ph)=N–NH–Ph as a function of the R2 = Ph torsion angle and in comparison with the total energy.

Table 4 B3LYP/6-311+G(2d,p) chemical shifts (in ppm) of H_α and H_β of the hydrazonic carbon in the *Z* and *E* conformers of Et–C(Ph)=N–NH–Ph as a function of the $NCC_\alpha(Et)C_\beta(Et)$ torsion angle. ΔE represents the total energy relative to the equilibrium for a given conformer. The chemical shifts have been scaled by 0.95

			δ	
	θ/°	ΔE/kcal mol^{-1}	H_α	H_β
E				
	60.0	3.7	2.81	1.38
	82.5	0.0	2.54	1.19
	100.0	2.1	2.48	1.40
Z				
	95.0	0.4	2.60	0.98
	114.2	0.0	2.66	0.86
	135.0	0.8	2.70	0.79

equilibrium values. Together with the total energy, the evolution of δ with θ is sketched in Figs. 2 and 3 for the *E* and *Z* conformers, respectively. For the *E* isomer, equilibrium corresponds to θ = 165° and the torsion potential is steeper when going towards smaller θ values than when θ increases. Fluctuations in θ are therefore expected to lead to a small increase in $\delta(H_\alpha)$ and a small decrease in $\delta(H_\beta)$. This increase in $\delta(H_\alpha)$ when θ approaches 180° is consistent with the deshielding effect of the phenyl ring (R2) on the nuclei belonging to the same plane whereas the H_β experiences a shielding effect. The opposite situation occurs for the *Z* isomer. In addition, we investigated the effect of Et rotation upon δ while freezing all the other geometrical parameters (Table 4). In the case of the *E* isomer, rotation is hampered by the steric interactions between the R1 = Et and R = Ph groups so that ΔE increases strongly when changing θ. In contrast, the Et group has more freedom to move in the *Z* isomer. However, variations in θ have a negligible effect upon $\delta(H_\alpha)$ and $\delta(H_\beta)$. These simulations also confirm the larger $\delta(H_\alpha)$ for the *E* isomer of the R1 = Et compound than for its *Z* conformer and therefore the permutation in the assignment by Bellamy and Hunter. Consequently, fluctuations in the dihedral angles associated with the Et and Ph torsions cannot account for the large difference between theory and experiment for $\delta(H_\alpha)$ when R1 = Et is in the *syn* position with respect to the NH–Ph group. This large difference for the *E* isomer can however be traced back to the solvent (benzene) employed by Bellamy and Hunter[10] for the R1 = Et compound whereas CCl_4 was used for the other systems. Indeed, Karabatsos[9] explained that benzene molecules can interact with the H(N) of the hydrazone to form H-bonded complexes, which leads to important shielding effects on H_α. This is supported by the variation of $\delta(H_\alpha)$ in the parent (R1 = Me, R2 = Ph) phenylhydrazone from 2.00 to 1.47 when replacing the CCl_4 solvent by benzene.

IV Conclusion

Ab initio GIAO calculations of chemical shifts have been carried out in order to interpret the experimental ^{1}H NMR spectra of the *E* and *Z* isomers of alkyl phenyl ketone phenylhydrazones R1–C(Ph)=N–NH–Ph (R1 = Me, Et, iPr, and tBu). For R1 = Me, Karabatsos' rule[9] is verified, *i.e.* $\delta(H_\alpha)$ is smaller when the R1 group is in the *syn* position with respect to the NH–Ph group (*E* isomer). For R1 = iPr and tBu, substantiating the assignment of Bellamy and Hunter,[10] the reverse situation occurs and both $\delta(H_\alpha)$ and $\delta(H_\beta)$ are larger when the R1 group is in the *syn* position with respect to the NH–Ph group. This results from the relative positions of the substituents (R1 = iPr, tBu and R2 = Ph) of the hydrazonic carbon and their impact on the positions of H_α and H_β with respect to the shielding and deshielding cones of the R2 = Ph ring. Indeed, in the *Z* conformer, as a result of steric interactions between these substituents as well as between the NH group and the phenyl ring, the torsion of the R2 = Ph ring with respect to the C=N–NH plane is larger and affects the position of the hydrogen atoms of R1 in such a way they experience more positive shielding than in the *E* conformer. For the R1 = Et compound, of which the two isomers are almost present in equal proportions, a new assignment has been proposed, where only the chemical shifts of H_α satisfy Karabatsos' rule. Indeed, contrary to Bellamy and Hunter,[10] the signal associated with the H_β of the *Z* isomer appears at a higher field because, as a result of minimizing the steric interactions, the terminal Me group is oriented in the positive shielding cone of the benzene ring.

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References

1 J. B. Lambert, W. L. Olivier and J. D. Roberts, *J. Am. Chem. Soc.*, 1965, **87**, 5085; G. J. Karabatsos and S. S. Lande, *Tetrahedron*, 1968, **24**, 3097; H. Kessler and D. Leibrift, *Tetrahedron Lett.*, 1969, 427; H. Kessler and D. Leibrift, *Tetrahedron*, 1969, **25**, 5127; F. Kerek, G. Ostrongovich and Z. Simon, *J. Chem. Soc. (B)*, 1971, 451.
2 D. Y. Curtin, E. J. Grubbs and C. G. Mc Carty, *J. Am. Chem Soc.*, 1966, **88**, 2775; G. J. Karabatsos and N. Hsi, *Tetrahedron*, 1967, **23**, 1079; G. J. Karabatsos and R A. Taller, *Tetrahedron*, 1968, **24**, 3347; H. Kessler and D. Leibrift, *Tetrahedron*, 1970, **26**, 1805; G. E. Hawkes, K. Herwing and J. D. Roberts, *J. Org. Chem.*, 1974, **39**, 1017; M. Allen and J. D. Roberts, *J. Org. Chem.*, 1980, **45**, 130.
3 R. H. Moriarty, C. L. Yeh, K. C. Ramey and P. W. Whitehurst, *J. Am. Chem. Soc.*, 1970, **92**, 6360.

4 G. J. Karabatsos, J. D. Graham and F. M. Vane, *J. Am. Chem. Soc.*, 1961, **84**, 753; G. J. Karabatsos, B. L. Shapiro, J. S. Fleming and J. S. Ratka, *J. Am. Chem. Soc.*, 1963, **85**, 2784; G. J. Karabatsos, F. M. Vane, R A. Taller and N. Hsi, *J. Am. Chem. Soc.*, 1964, **86**, 335; C. I. Stassinopoulou, C. Zioudrou and G. J. Karabatsos, *Tetrahedron Lett.*, 1972, **35**, 3671.
5 J. H. Davies, R. H. Davies and P. Kirby, *J. Chem. Soc. (C)*, 1968, 431; R. Blaser, P. Infeld and O. Schindler, *Helv. Chem. Acta*, 1969, **52**, 569; O. Exner and O. Schindler, *Helv. Chem. Acta*, 1969, **52**, 577.
6 M. F. Betkouski and W. Lwowski, *J. Chem. Soc., Perkin Trans. 1*, 1973, 932.
7 M. Chihaoui and B. Baccar, *C. R. Acad. Sci. Paris, t, Ser. C*, 1978, 69.
8 F. Chabchoub, M. Trabelsi and M. Salem, *J. Soc. Chim. Tunis.*, 1998, **3**, 171.
9 G. J. Karabatsos and R. A. Taller, *J. Am. Chem. Soc.*, 1963, **85**, 3624.
10 A. J. Bellamy and J. Hunter, *J. Chem. Soc., Perkin Trans. 1*, 1976, 456.
11 R. Ditchfield, *J. Am. Chem. Soc.*, 1971, **93**, 5287; R. Ditchfield, *Mol. Phys.*, 1974, **27**, 789; K. Wolinski, J. F. Hilton and P. Pulay, *J. Am. Chem. Soc.*, 1990, **112**, 8251.
12 R. Benassi and F. Taddei, *J. Chem. Soc., Perkin Trans. 2*, 1985, 1629.
13 E. El-Taher and A. A. Salem, *Struct. Chem.*, 1998, **9**, 169.
14 A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648.
15 P. C. Hariharan and J. A. Pople, *Theor. Chim. Acta*, 1973, **28**, 213; M. M. Francl, W. J. Pietro, W. J. Hehre, J. S. Binkley, M. S. Gordon, D. J. DeFrees and J. A. Pople, *J. Chem. Phys.*, 1982, **77**, 3654.
16 B. A. Hathaway, G. Day, M. Lewis and R. Glaiser, *J. Chem. Soc., Perkin Trans. 2*, 1998, 2713.
17 S. J. Vosko, L. Wilk and M. Nusair, *Can. J. Phys.*, 1980, **58**, 1200.
18 C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B*, 1988, **37**, 785.
19 J. C. Slater, *Phys. Rev.*, 1951, **81**, 385.
20 A. D. Becke, *Phys. Rev. A*, 1988, **38**, 3098.
21 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. P. Liashenko, A. P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. G. Johnson, W. Chen, M. W. Wong, J. L. Andres, M. Head-Gordon, E. S. Replogle and J. A. Pople, GAUSSIAN 98, Revision A11, Gaussian Inc., Pittsburgh, PA, 1998.
22 D. B. Chesnut, *Rev. Comput. Chem.*, 1996, **8**, 245.
23 P. R. Rablen, S. A. Pearlman and J. Finkbiner, *J. Phys. Chem. A*, 1999, **103**, 7357.
24 R. Cammi, B. Mennucci and J. Tomasi, *J. Chem. Phys.*, 1999, **110**, 7627.
25 T. Helgaker, M. Jaszunski and K. Ruud, *Chem. Rev.*, 1999, **99**, 293.
26 K. Ruud, P. O. Åstrand and P. R. Taylor, *J. Am. Chem. Soc.*, 2001, **123**, 4826.
27 T. M. Nymand, P. O. Åstrand and K. V. Mikkelsen, *J. Phys. Chem. B*, 1997, **101**, 4105.
28 C. Reichardt, *Solvent and Solvent Effects in Organic Chemistry*, VCH, Weinheim, 1990, Section 4.4.
29 C. J. F. Böttcher, *Theory of Electric Polarization*, Elsevier, Amsterdam, 1973, vol. I, p. 145.
30 R. Knorr, *Chem. Ber.*, 1980, **113**, 2441.