Interplay between steric and electronic factors in determining the strength of intramolecular resonance-assisted NH···O hydrogen bond in a series of β-ketoarylhydrazones

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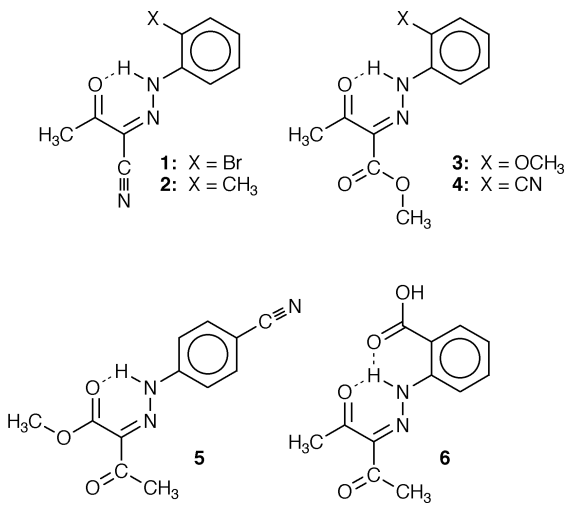
The crystal structures of six β-ketoarylhydrazones are reported: **1**,(*Z*)-2-(2-bromophenylhydrazono)-3-oxobutanenitrile; **2**, (*Z*)-2-(2-methylphenylhydrazono)-3-oxobutanenitrile; **3**, (*E*)-methyl-2-(2-methoxyphenylhydrazono)-3-oxobutanoate; **4**, *E*, methyl-2-(2-cyanophenylhydrazono)-3-oxobutanoate; **5**, (*Z*)-methyl-2-(4-cyanophenylhydrazono)-3-oxobutanoate; **6**, pentane-2,3,4-trione-3-(2-carboxyphenylhydrazone). All of them form intramolecular hydrogen bonds assisted by resonance (RAHB), with N···O distances in the range 2.541(5)–2.615(3) Å. These hydrogen bonds are differently affected by the substituents at the heterodienic fragment, being strengthened by electronwithdrawing substituents in position 2 (more by 2-COMe than 2-CN substitution), and weakened in β-esterhydrazones and when the N–H forms a bifurcated hydrogen bond. The role played by the different steric and electronic properties of the substituents in strengthening the H-bond is investigated, besides X-ray crystallography, by IR and ^{1}H NMR characterization of the NH proton, and quantum mechanical DFT calculations at the B3LYP/6-31 + G(d,p) level of theory on test molecules.

In recent years much attention has been devoted to structural studies of heterodienic systems forming strong intramolecular N–H···O hydrogen bonds assisted by resonance (RAHB) which, *inter alia*, could have potential technological applications as bistate molecular switches.[1–6] This paper reports the crystal structures of a series of six β-ketoarylhydrazones that form such intramolecular H-bonds and represents an extension of our previous work[3,4] on two strictly homogeneous series of β,β′-diketoarylhydrazones with intramolecular N···O distances as short as 2.55 Å. The present compounds (Scheme 1) include two β-keto-β′-cyanohydrazones, **1** and **2**, three β-keto-β′-esterhydrazones, **3**, **4** and **5**, and one β,β′-diketohydrazone, **6**, all of them containing at least one HN–N=C–C=O heterodienic system with the correct geometry to form intramolecular N–H···O RAHBs. The general problem of resonant heteronuclear N–H···O bonds is that, at variance



Scheme 1

with homonuclear O–H···O RAHBs,[7–9] their bond strength, intended as N···O contact distance, is spread over a much wider range and appears to depend, besides π-delocalization, on the nature of the substituents on the heterodienic moiety. This fact can tentatively be interpreted by noting that: (*i*) while the heteronuclear X–H···Y RAHB is intrinsically weaker than the X–H···X homonuclear one because the difference between the proton affinities (PA) of H-bond donor and acceptor atoms hinders efficient mixing of the X–H···Y↔X···H–Y resonance forms, (*ii*) it can be, however, made stronger by the presence of chemical substituents able to reduce such a PA difference. Because of the variety of their substituents, the present compounds give an opportunity to define the role played by steric and electronic factors in determining the N–H···O H-bond strength. This problem is tackled here by different methods, including X-ray crystal structure determinations, IR and NMR characterizations of the N–H proton, and high-level quantum mechanical calculations on model compounds.

Results and discussion

Description of the structures

A selection of bond distances and bond angles is given in Table 1. Table 2 reports the hydrogen bond parameters and Table 3 Pauling's bond orders[10] and π-delocalization parameters for the β-ketohydrazone moieties. ORTEP[11] views of the molecules, projected on the mean hydrazone plane, are shown in Figs. 1–6.

The two β-keto-β′-cyanoarylhydrazones (**1** and **2**) both have the *Z* configuration and display intramolecular N–H···O bonds with N···O distances of 2.594(3) and 2.596(3) Å. These fall on the long side of the N···O distance range of 2.55–2.61 Å observed in the previously studied series of β,β′-diketoarylhydrazones,[3,4] suggesting that the cyano group is less

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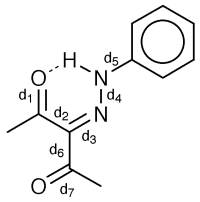
Table 1 Selected bond lengths (Å) and angles (°) for the crystal structures of compounds **1**–**6** (e.s.d.s in parentheses)



	d_1	d_2	d_3	d_4	d_5	d_6	d_7
1	1.212(4)	1.468(5)	1.310(4)	1.303(4)	1.397(3)		
2	1.229(3)	1.453(4)	1.330(3)	1.300(3)	1.404(3)		
3	1.224(3)	1.466(2)	1.319(3)	1.299(3)	1.397(3)	1.481(3)	1.198(3)
4	1.222(4)	1.469(5)	1.317(4)	1.295(3)	1.402(5)	1.475(4)	1.199(5)
5	1.211(3)	1.474(4)	1.300(4)	1.309(3)	1.401(3)	1.489(4)	1.204(4)
6a	1.223(3)	1.471(3)	1.308(3)	1.318(3)	1.399(3)	1.488(4)	1.207(3)
6b	1.221(3)	1.469(3)	1.322(3)	1.309(3)	1.405(2)	1.494(4)	1.203(3)
	d_1–d_2	d_2–d_3	d_3–d_4	d_4–d_5	d_2–d_6	d_3–d_6	d_6–d_7
1	119.1(3)	126.7(3)	119.3(3)	120.1(2)			
2	119.5(2)	127.0(2)	118.3(2)	120.6(2)			
3	118.9(2)	124.6(2)	120.7(3)	119.6(2)	121.3(2)	114.1(2)	124.7(2)
4	118.6(4)	124.2(3)	120.7(3)	119.8(3)	122.2(3)	113.6(3)	125.7(3)
5	122.8(2)	122.1(2)	123.6(3)	119.3(2)	124.3(2)	113.6(2)	122.1(2)
6a	118.8(2)	124.5(2)	122.3(2)	118.0(2)	123.8(2)	111.8(2)	121.7(2)
6b	118.8(2)	124.6(2)	121.2(2)	118.3(2)	124.0(2)	111.4(2)	121.3(2)

efficient in strengthening the H-bond than the bulkier electron-withdrawing β′-keto substituent. The packing of compound **1** is dominated by the intermolecular Br···O1 contact of 3.077(2) Å [Fig. 1(*b*)], which is rather shorter than the sum of van der Waals radii of 3.37 Å.[12] Its geometry is that of a charge transfer complex[13] with electron donation from the oxygen lone pair to the empty π* orbital on the C–Br bond, an interaction often studied by crystallographic methods.[14] However, the C6–Br bond distance is not lengthened [1.888(3) Å to be compared with the standard one of 1.90(1) Å[15]] and this seems more indicative of a simple electrostatic interaction.[16]

Compounds **3** and **4** are β-keto-β′-esterarylhydrazones in the *E* configuration. They display intramolecular N–H···O bonds with N···O distances of 2.560(2) and 2.541(5) Å, respectively, which are strictly comparable with the shortest values previously observed[3,4] in β,β′-diketoarylhydrazones. The reasons for such a N···O strengthening are not easily understood. The C2=N2–N1 fragment is, by itself, heavily π-delocalized (on average 48% in compounds **1**–**4**; see Table 3) and the conjugation within the C4=O2 is clearly unable to increase it, as shown by the C2–C4 [1.481(3) in **3** and 1.475(4) Å in **4**] and C4=O2 [1.198(3) in **3** and 1.199(5) Å in **4**] distances, which correspond almost perfectly to C(sp^2)–C(sp^2)

Table 2 Hydrogen bonding parameters (Å, °) for the crystal structures of compounds **1**–**6** (e.s.d.s in parentheses)

	D–H···A	D–H	H···A	D···A	D–H···A
1	N1–H1···O1	0.75(3)	2.01(2)	2.594(3)	135(3)
2	N1–H1···O1	0.99(3)	1.76(3)	2.596(3)	140(2)
3	N1–H1···O1	0.88(2)	1.86(2)	2.560(2)	135(2)
	N1–H1···O4	0.88(2)	2.32(3)	2.616(2)	99(2)
4	N1–H1···O1	0.86(4)	1.96(5)	2.541(5)	124(4)
5	N1–H1···O2	0.85(3)	1.91(3)	2.615(3)	139(3)
6	N11–H11···O11	0.88(3)	1.95(2)	2.587(2)	128(2)
	N11–H11···O31	0.88(3)	2.02(3)	2.660(3)	129(2)
	O41–H41···O32	1.01(3)	1.64(3)	2.643(2)	173(3)
	N12–H12···O12	0.92(2)	1.93(2)	2.583(3)	127(2)
	N12–H12···O32	0.92(2)	1.96(2)	2.657(3)	131(2)
	O42–H42···O31	0.95(3)	1.71(3)	2.662(2)	177(3)

Table 3 Pauling's bond orders and conjugation parameters within the ketohybrazone moieties for the crystal structures of compounds **1**–**6** (e.s.d.s in parentheses). The π-delocalizations were evaluated in terms of the Pauling bond order[10] n in the two separate O=C–C and C=N–NH subfragments as: $\eta_{1,2} = 1/2[(2 - n_1) + (n_2 - 1)]$ and $\eta_{3,4} = 1/2[(2 - n_3) + (n_4 - 1)]$ where $\eta_{1,2}$ and $\eta_{3,4}$ are, by definition, equal to 0 and 1 for the non-delocalized systems, HN–N=C–C=O and HN^+=N–C=C–O^-, respectively, and 0.5 for the fully π-delocalized system

	n_1	n_2	n_3	n_4	$\eta_{1,2}$	$\eta_{3,4}$
1	1.91	1.10	1.64	1.50	0.10	0.43
2	1.79	1.17	1.49	1.52	0.19	0.52
3	1.82	1.11	1.57	1.52	0.14	0.48
4	1.84	1.10	1.59	1.55	0.13	0.48
5	1.92	1.07	1.72	1.45	0.08	0.36
6a	1.83	1.09	1.66	1.40	0.13	0.37
6b	1.84	1.10	1.55	1.49	0.13	0.50

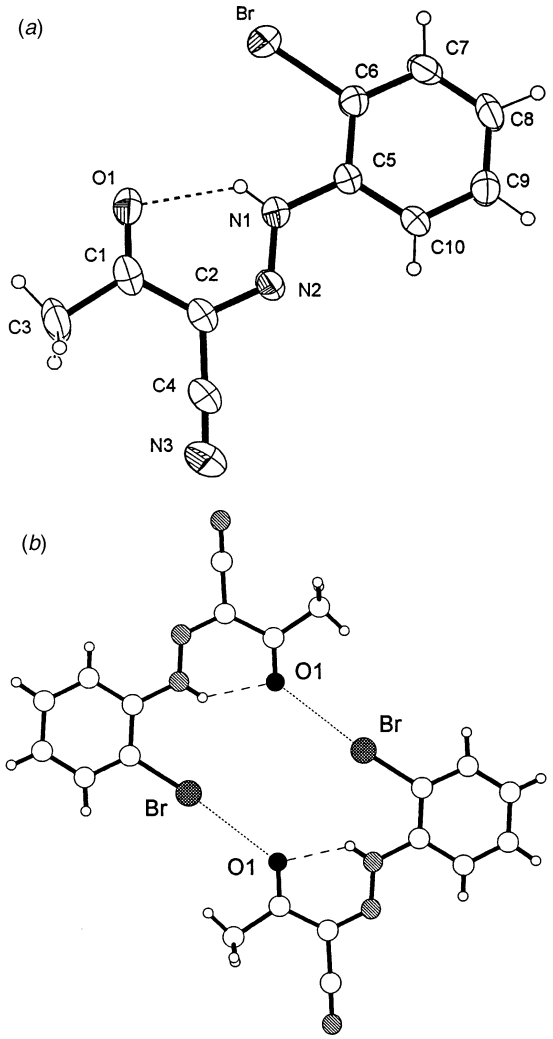


Fig. 1 (*a*) ORTEP view and atom numbering for compound **1**. (*b*) Electrostatic short interaction between Br and O1 of the C1=O1 carbonyl group.

single and C(sp^2)=O double bonds, respectively. This does not exclude that the electron-withdrawing –COOR group may strengthen the hydrogen bond by increasing the N–H proton acidity (*i.e.*, by decreasing the nitrogen PA; *vide supra*) for a purely electrostatic (inductive) effect (Hammett $\sigma_I = 0.35$ for –COOR).[17] In this case, however, the more electron-withdrawing –CN ($\sigma_I = 0.61$) should produce even shorter hydrogen bonds in **1** and **2**, in disagreement with what is actually observed. The other hypothesis is that the –COOR

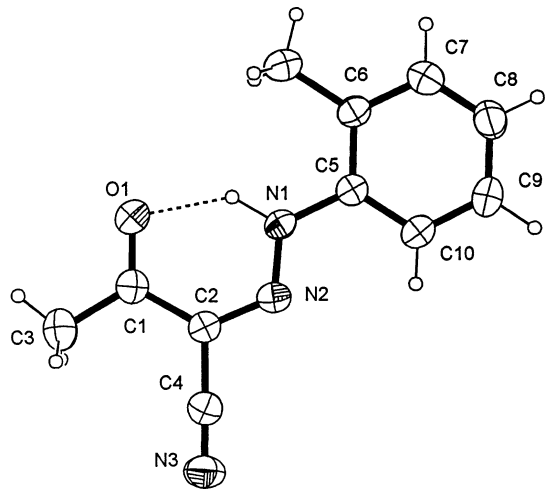


Fig. 2 ORTEP view and atom numbering for compound **2**.

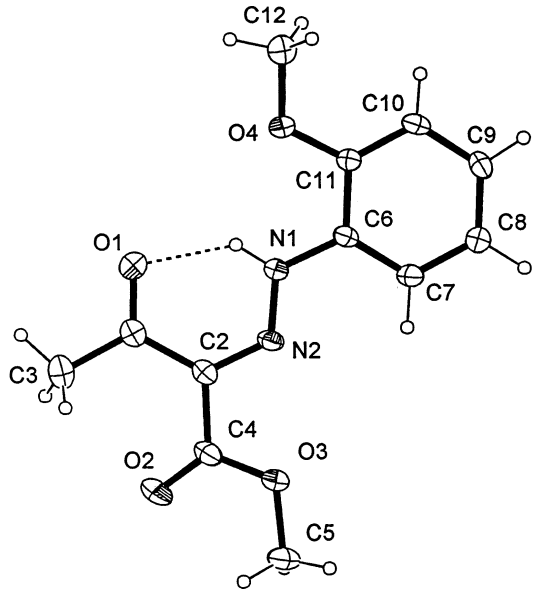


Fig. 3 ORTEP view and atom numbering for compound **3**.

group shortens the bond by shrinking the C–C=N angle in *ipso* because of steric repulsion. This is supported by the values of the C1–C2=N2 internal angle, which are 126.7(3)° and 127.0(2)° in **1** and **2**, and which decrease to 124.6(2)° and 124.2(3)° in **3** and **4** as a consequence of the substitution of the –CN by the –COOMe group. This idea is in line with the fact

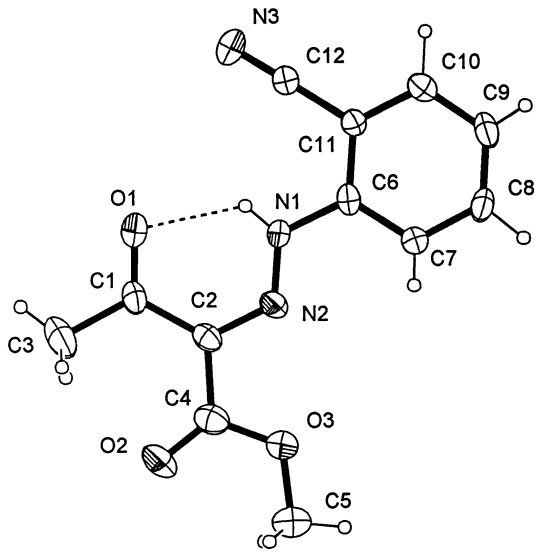


Fig. 4 ORTEP view and atom numbering for compound **4**.

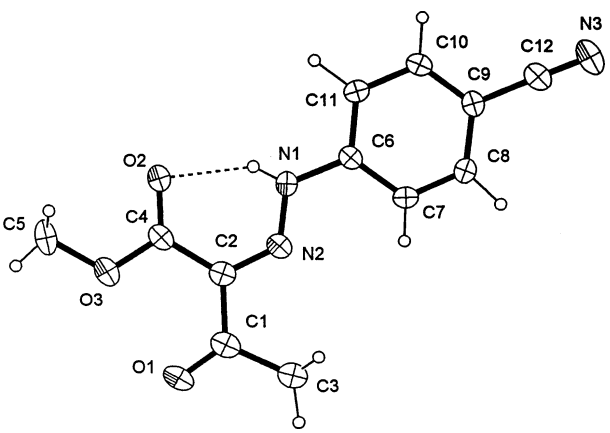


Fig. 5 ORTEP view and atom numbering for compound **5**.

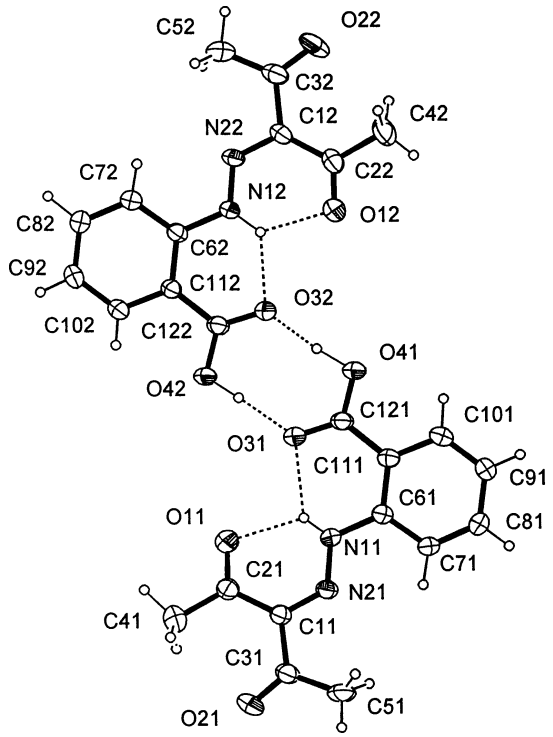


Fig. 6 ORTEP view and atom numbering for the dimeric asymmetric unit of compound **6**.

that the H-bonded six-membered ring is highly strained at the C2 atom, as shown by comparison to the corresponding C1–C2=N2 angles in the zig-zag planar form of six *anti*-β-ketohydrazones, which are, on average, 119.4(4)°.[18]

The β-keto-β′-esterarylhydrazone **5** displays a *Z* configuration and N···O contact distance of 2.615(3) Å, longer than those observed in compounds **3** and **4**. The expected methoxyl effect should be in the opposite direction, that is of closing the H-bonded ring for steric hindrance as shown by the widening of the C1–C2–C4 angle [124.3(2)° in **5** against 121.3° and 122.2° in **3** and **4**, respectively] because of O1···O3 interatomic repulsion. This indicates that the H-bond length is not only determined by steric factors, but also by electronic ones, in this case the specific properties of the esteric functionality, which is already known to produce both a weakening of the intramolecular RAHB in crystals[7,9] and to decrease of the percent enolization in solution[19] of β-diketone enols. The H-bond lengthening against the O1···O3 repulsion is accompanied by a concurrent widening of the O2=C4–C2 and N1–N2=C2 internal angles to their actual values of 122.8(3)° and 123.6(3)°, to be compared with the corresponding values in **3** and **4** (on average 118.7° and 120.7°, respectively).

Compound **6** is a β,β′-diketoarylhydrazone with two independent molecules in the asymmetric unit linked into dimers by two carboxylic H-bonds [O···O = 2.643(2) and 2.662(2) Å] around a non-crystallographic centre of symmetry. In view of its formula, **6** could be expected to form an intramolecular RAHB as short as those found in compounds **3** and **4**. In fact, the actual H-bond observed is rather longer [N···O = 2.587(2) and 2.583(2) Å] because of the weakening effect[20] of the N–H bond bifurcation with the carboxylic group in the *ortho* position on the phenyl.

In conclusion, crystallographic data show that the intramolecular H-bond in β-ketohydrazones is remarkably shortened (up to 2.54 Å) with respect to other N–H···O bonds in cyclic systems where π-conjugation is impossible (*e.g.*, N···O = 2.996–3.210 Å in intramolecularly H-bonded triamides[21]). This seems a clear indication that the present H-bonds are strengthened by the RAHB mechanism. These H-bonds are, moreover, affected in a different way by the nature of the substituents, being strengthened by electron-withdrawing substituents in position 2 (more by 2-CO than 2-CN substitution), weakened in β-"esterhydrazones", and possibly strengthened by bulky substituents in position 1.

Spectroscopic data

Hydrogen bonds as short as 2.54–2.61 Å are expected to produce a lengthening of the N–H bond with respect to that unperturbed by hydrogen bonding (1.009 and 1.0116 Å from neutron diffraction[15] and gas electron diffraction, respectively[22]). Unfortunately, X-ray crystallography is unable to locate proton positions with sufficient accuracy and all *d*(N–H) values fall in the much shorter range of 0.75–0.99 Å. This N–H lengthening, however, can be appreciated by both NMR and IR measurements (Table 4). Weak N–H···O bonds are known to give δ(NH) values in the range 7–9 ppm. Values presently observed are ~15 ppm for the stronger H-bonds in **1**–**4** and 12.70 ppm for the weaker bond in **5,** while the chemical shift goes up to 15.47 ppm for the bifurcated (three-center) H-bond in **6**. This is a clear indication of some N–H lengthening, as confirmed by the values of the IR stretching frequencies. These are known to be around 3400 cm^{-1} for the free N–H group and in the range 3200–3400 cm^{-1} for N–H groups involved in non-resonant H-bonds. Data of Table 4 indicate greater shifts down to 2950 cm^{-1} with a nearly linear dependence of the *v*(NH) *vs.* *d*(N···O) relationship.

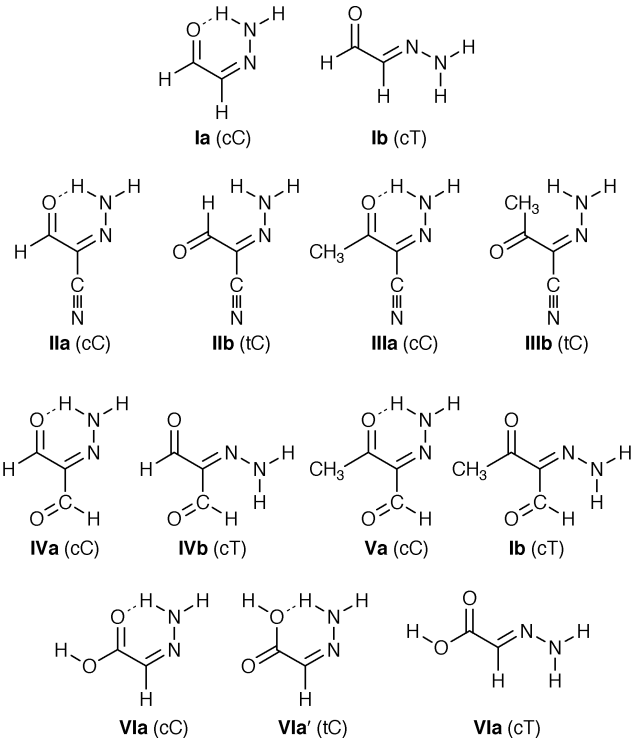
Quantum mechanical calculations

Crystallographic and spectroscopic experimental findings have been submitted to verification by DFT calculations of sufficient accuracy (see experimental part for details) on model compounds having the appropriate structures for discriminating among the different steric and electronic perturbation factors. These calculations, moreover, are intended to evaluate H-bond energies, E_{HB}, by looking at the difference of the absolute energies of the *open* (non H-bonded) and *closed* (H-bonded) forms of the same compound. Scheme 2 collects the *closed* and *open* geometries of all the test molecules considered. Molecules chosen are the simple β-ketohydrazone **I**, its 2-CN and 2-COH substituted derivatives **II** and **IV** and, to evaluate the role of steric factors, the 1-CH_3 derivatives **III** and **V** of the latter. The differences between keto and esterhydrazones are taken into account by the β-carboxyhydrazone **VI** and, finally, the global effect of resonance by the non-resonant H-bonded form **VIa′**. To reduce the amount of calculations the *N*-phenyl substitution has not been considered. Preliminary calculations on the pair β-ketohydrazone–*N*-phenyl-β-ketohydrazone have shown, however, that the intramolecular RAHB is only weakly affected by the presence of the phenyl group.

Results of the calculations are summarized in Table 5 as E_{HB} values, geometry of the N–H···O group and bond distances of the π-conjugated heterodiene. The values of the conjugation parameters $\eta_{1,2}$ and $\eta_{3,4}$ defined for the experimental structures in Table 3 are also reported. Direct comparison of N···O distances is possible between experimental **1** and **2** (on average 2.595 Å) and calculated **IIIa** (2.615 Å) values, and between experimental **3** and **4** (on average 2.550

Table 4 Spectroscopic data. IR stretching frequencies (cm^{-1}) and ^1H NMR chemical shifts (ppm) of the NH proton for compounds **1**–**6**

	N···O/Å	*v*(NH)	δ(NH)
1	2.594(3)	3050	14.87
2	2.596(3)	3050	14.97
3	2.560(2)	2950	14.92
4	2.541(2)	2950	15.10
5	2.615(3)	3170	12.70
6a	2.587(2)	3100	15.47
6b	2.583(2)		



Scheme 2

Å) and calculated **Va** (2.589 Å) values. The correspondence seems reasonable as is that between calculated η values (Table 5) and experimental values of Table 3. Calculations allow one to appreciate the N–H bond lengths that range from 1.010–1.011 Å for the *open* to 1.019–1.024 Å for the *closed* resonant forms. The H-bond remains strongly dissymmetric with $d(H\cdots O) \gg d(N–H)$ and the small NH lengthening observed is in line with the rather small decrease of the IR ν(NH) frequencies (Table 4).

The most simple β-ketohydrazone **Ia** gives an intramolecular H-bond having $d(N\cdots O) = 2.676$ Å and $E_{HB} = 29.41$ kJ mol^{-1}, which is only moderately strong in agreement with expectation. The effect of resonance on H-bond formation can be evaluated by comparing **Ia** (the simplest RAHB-forming β-ketohydrazone) with **VIa′**, a molecule containing the same number of sp^2 atoms intramolecularly H-bonded, but where π-conjugation is interrupted: the N···O distance in the non-resonant molecule is slightly longer (2.697 against 2.676 Å), but E_{HB} drops to 7.03 kJ mol^{-1}. The decrease (22.38 kJ mol^{-1}) may be taken as the synergistic contribution of resonance to the setting up of the intramolecular H-bond. Similar conclusions were drawn by Dannenberg and Rios,[23] who apportioned the intramolecular H-bond energy of 50.20 kJ mol^{-1} calculated for the enol form of acetylacetone into 25.10 kJ mol^{-1} due to H-bonding and 25.10 kJ mol^{-1} due to the increase of resonance.

Comparison of **I**, **II** and **IV** shows that 2-substitution by electron-withdrawing substituents remarkably strengthens the H-bond formed, and more so for 2-CHO [$d(N\cdots O) = 2.651$ Å; $E_{HB} = 60.17$ kJ mol^{-1}] than for 2-CN [$d(N\cdots O) = 2.650$ Å; $E_{HB} = 44.64$ kJ mol^{-1}], in agreement with the experimental data. Model compounds **III** and **V** differ from **II** and **IV** as a further 1-methyl substitution is introduced to evaluate the effects of steric hindrance. These effects are not irrelevant because the N···O distance shrinks by 0.035 and 0.062 Å in **IIIa** and **Va**, respectively, while both H-bond energies increase by some 7–9 kJ mol^{-1}.

Finally, quantum mechanical calculations confirm the experimental observation that β-esterhydrazones give systematically weaker RAHBs than β-ketohydrazones, as shown by the β-carboxyhydrazone **VIa**, which displays both longer N···O distance (2.702 Å) and weaker E_{HB} (22.26 kJ mol^{-1}) than the corresponding β-ketohydrazone **Ia**.

Conclusions

Crystal structure data show that the mechanism of Resonant Assisted Hydrogen Bonding (RAHB) suggested for ···O=C–C=C–OH··· β-diketone enols[7–9] is still working for the formally equivalent π-conjugated ···O=C–C=N–NH··· β-ketohydrazone fragment and that specific substituents at the two carbon atoms may produce consistent variations of the RAHB efficacy (in the order 2-COOR > 2-CN ≫ 1-OR) that are to be largely imputed to specific electronic effects. Crystal data results are perfectly paralleled by the values of NMR δ(NH) chemical shifts and FTIR ν(NH) stretching frequencies.

Theoretical DFT calculations on test molecules, differently substituted at the C atoms, allow one to evaluate the corresponding H-bond energies, which turn out to be 29.4 kJ mol^{-1} for the unsubstituted ketohydrazone, and 60.2, 44.7 and 22.3 kJ mol^{-1} for the 2-CHO, 2-CN and 1-OH substituted derivatives, energies that can be increased by some 7–9 kJ mol^{-1} because of steric compression. The relevance of resonance in strengthening the N–H···O bond is stressed by the low H-bond energy value of only 7.0 kJ mol^{-1} obtained for a similar H-bonded six-membered ring in which the fragment π-conjugation has been interrupted.

Experimental and calculations

Crystallography

Compounds **1**–**5** were obtained by coupling diazonium ions with methyl-3-aminocrotonate and 3-aminocrotonitrile. Details of the synthesis were reported elsewhere.[24] Compound

Table 5 DFT optimized geometries of some intramolecularly hydrogen-bonded (*closed*) and non-hydrogen-bonded (*open*) test molecules depicted in Scheme 2, and their conjugation parameters η (see Table 3). Hydrogen bond energies (kJ mol^{-1}) are calculated as differences between the *open* and *closed* form energies. All calculations at the B3LYP/6-31 + G(d,p)//B3LYP/6-31 + G(d,p) level of theory. ZPE corrections (not applied) are of the order of 2.93 kJ mol^{-1}, as evaluated by the simplest term of the series

	E_{HB}	N···O	N–H	H···O	N–H···O	C=O	C–C	C=N	N–N	$\eta_{1,2}$	$\eta_{3,4}$
Ia	29.41	2.676	1.021	1.915	128.8	1.238	1.450	1.313	1.313	0.28	0.40
Ib			1.010			1.219	1.472	1.294	1.321	0.16	0.29
IIa	44.64	2.650	1.023	1.887	128.8	1.232	1.465	1.323	1.302	0.22	0.48
IIb			1.010			1.216	1.480	1.310	1.312	0.14	0.40
IIIa	54.18	2.615	1.023	1.851	128.6	1.237	1.481	1.321	1.302	0.22	0.48
IIIb			1.010			1.220	1.505	1.306	1.314	0.10	0.40
IVa	60.17	2.651	1.024	1.883	129.2	1.234	1.464	1.323	1.302	0.24	0.48
IVb			1.011			1.216	1.494	1.311	1.309	0.11	0.41
Va	67.40	2.589	1.024	1.820	128.9	1.240	1.485	1.325	1.300	0.22	0.50
Vb			1.011			1.220	1.521	1.313	1.309	0.08	0.42
VIa	22.26	2.702	1.019	1.962	127.1	1.231	1.460	1.304	1.317	0.24	0.36
VIa′	7.03	2.697	1.015	2.004	123.3	1.216	1.470	1.300	1.320	0.16	0.33
VIb			1.011			1.214	1.473	1.290	1.323	0.15	0.28

Table 6 Crystal data

	1	2	3	4	5	6
Formula	$C_{10}H_8BrN_3O$	$C_{11}H_{11}N_3O$	$C_{12}H_{14}N_2O_4$	$C_{12}H_{11}N_3O_3$	$C_{12}H_{11}N_3O_3$	$C_{12}H_{12}N_2O_4$
M	266.10	201.23	250.25	245.24	245.24	248.24
System	Monoclinic	Orthorhombic	Monoclinic	Triclinic	Orthorhombic	Monoclinic
Space group	$P2_1/c$	$Pbca$	$P2_1/n$	P-1	$Pbcm$	$P2_1/n$
a/Å	11.263(2)	7.565(2)	12.720(2)	8.302(1)	12.651(2)	11.411(2)
b/Å	6.863(2)	14.423(2)	6.954(1)	8.516(2)	14.571(2)	13.828(3)
c/Å	14.267(2)	19.793(3)	14.783(3)	9.333(2)	6.649(1)	15.143(2)
α/°	90	90	90	99.50(2)	90	90
β/°	94.01(1)	90	111.61(1)	97.06(2)	90	98.45(1)
γ/°	90	90	90	108.21(2)	90	90
U/Å^3	1100.1(4)	2159.6(7)	1215.7(4)	607.4(2)	1225.7(3)	2363.5(7)
Z	4	8	4	2	4	8
T/K	295	295	295	295	295	295
μ/cm^{-1}	37.13	0.83	1.04	0.99	0.98	1.07
Unique reflns.	2643	2580	2633	2511	1595	5125
Obs. reflns [$I > 2\sigma(I)$]	1287	940	1711	1170	1056	2517
R_1 (obs. reflns.)	0.041	0.057	0.049	0.072	0.054	0.054
wR_2 (all reflns.)	0.088	0.131	0.141	0.199	0.175	0.142
R_{int}	0.011	—	0.016	0.030	—	0.031

6 was prepared by coupling acetylacetone with a substitute diazonium salt.[25] Compounds **1**, **2** and **4** were recrystallized from an ethyl acetate–acetonitrile mixture; **3** and **5** from ethyl acetate; **6** from ethanol. All X-ray diffraction data were collected at room temperature on an Enraf-Nonius CAD-4 diffractometer using graphite-monochromated Mo Kα radiation ($\lambda = 0.710\,69$ Å) with an $\omega/2\theta$ scan technique. Lattice constants were determined by least-squares fitting of the setting angles of 25 reflections. Intensities of three standard reflections were measured every 2 h and did not show significant variations for any of the six compounds investigated. All intensities were corrected for Lorentz and polarization effects. Scattering factors were taken from Cromer and Waber.[26] The structures were solved by direct methods using the SIR92[27] system of programs and all other calculations were accomplished using SHELXL-97[28] and PARST.[29] All structures were refined on F^2 by full-matrix least-squares methods with anisotropic non-H atoms and isotropic hydrogens. Crystal data are reported in Table 6.

CCDC reference number 440/146. See http://www.rsc.org/suppdata/nj/1999/1261/ for crystallographic files in cif format.

IR and NMR spectra

IR spectra were recorded on a Nicolet 510P FT-IR spectrometer on KBr pellets and ^{1}H NMR on a Gemini 300 VARIAN in $CDCl_3$ solution (25 °C).

Computational details

It is known since 1985[30] that the H-bond geometry of RAHB molecules cannot be reproduced at the Hartree–Fock level. Conversely, geometry optimizations carried out by *ab initio* Møller–Plesset[31] MP2 methods and 6-31G(d,p) basis sets (or larger) have given good agreement with experiments for the O–H···O intramolecular RAHB of malondialdehyde,[30,32] acetylacetone,[23] 3-formylmalondialdehyde[33] and 3-formylacetylacetone.[33] The problem of the basis set choice in strong H-bonds, also called low-barrier H-bonds (LBHB),[34] has been investigated systematically by McAllister and coworkers,[35] who conclude "that, on the basis of geometrical analysis, 6-31+G(d,p) is the best basis set for the general study of LBHBs", and that *ab initio* Møller–Plesset methods at the MP2, MP3 and MP4 level give substantially the same results among themselves and with respect to the density functional theory (DFT) methods B3LYP and BLYP.[36] In view of these considerations and of the fact that DFT geometry optimizations are rather faster than the MP2 ones (some four times for our molecules), all calculations were accomplished by using the Gaussian 94[37] suite of programs at the B3LYP/6-31 + G(d,p)// B3LYP/6-31 + G(d,p) level of theory with full geometry optimization in point group C_s. H-bond energies, E_{HB}, have been evaluated as the energy difference between non-H-bonded (**cT** : *cis-Trans* or **tC** : *trans-Cis*) structures and H-bonded (**cC** : *cis-Cis*) forms (see Scheme 2). By convention, we have chosen to refer E_{HB} to the **cT** form (whenever possible) because it conserves the maximum number of non-bonded interactions of the **cC** form. The E_{HB} so defined is to be corrected for the effects of ZPVE (zero point vibrational energy). For the sake of simplicity, the vibrational contribution has been evaluated only for the B3LYP treatment of simple ketohydrazone **I**; it is found that ZPVE systematically lowers E_{HB} by some 2.93 kJ mol^{-1}.

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Paper 9/061111H