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Solution and solid state structure and tautomerism of azo coupled enaminone derivatives of benzoylacetone

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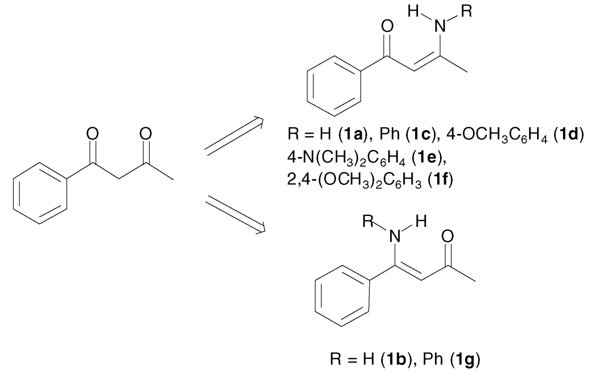
The reaction of 4-substituted benzenediazonium tetrafluoroborates with 3-amino-1-phenylbut-2-en-1-one, 4-amino-4-phenylbut-3-en-2-one and their *N*-aryl derivatives **1a–1g** has been used to prepare the respective azo coupling products *i.e.* compounds **2–5** from enaminone **1a**, compounds **6–9** from enaminone **1c**, compound **10** from enaminone **1d**, compound **11** from enaminone **1e**, compounds **12, 13** from enaminone **1f**, compounds **14, 15** from enaminone **1b** and compound **16** from enaminone **1g**. Tautomerism of the azo coupling products prepared has been investigated in $CDCl_3$ solutions by means of ^1H, ^{13}C and ^{15}N NMR spectra. Crystal structures of selected products have also been investigated by means of X-ray diffraction.

Introduction

In previous papers, we described tautomeric behaviour of the products formed by reactions of diazonium salts with enaminones of various kinds. 4-Arylaminopent-3-en-2-ones are the first amino-group-carrying substrates that produce hydrazones by reactions with diazonium salts.[1,2] On the other hand, 4-amino- and 4-(methylamino)pent-3-en-2-ones are the first aliphatic substrates to produce azo compounds by azo coupling reactions.[1] The tautomerism of these substances in solution is connected with restricted rotation around the polarized C=C double bond. [1,3] Generally, so far it has been established that the tautomeric form of the products of azo coupling reactions with β-enaminones depends first of all on the type of amino group (primary, secondary, tertiary) and on substituents at the amino group (methyl, aryl).[1–5] The 4-aminopent-3-en-2-ones with primary and secondary amino groups react with one equivalent of diazonium salt only but 4-(dimethylamino)pent-3-en-2-one reacts with two equivalents of diazonium salt at two different carbon atoms[5] (in contrast to the formation of formazanes in the reactions of methylketones). Also some substituted 3-amino-5,5-dimethylcyclohex-2-en-1-ones react like 4-(dimethylamino)-pent-3-en-2-one.[6]

The enaminones characterised so far were prepared from symmetrical β-diketones (acetylacetone, dimedone). Unsymmetrical β-diketones (*e.g.* benzoylacetone) can form two types of enaminones (for the case of benzoylacetone, see Scheme 1).



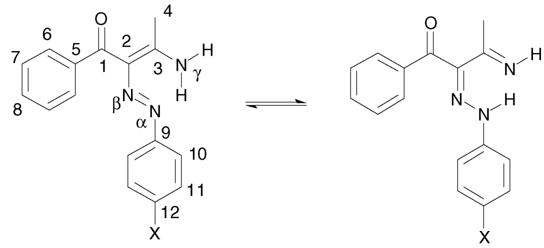
Scheme 1

As the structure and behaviour of enaminones are affected by the type of groups in the vicinity of the carbonyl or enamino groups,[7] we decided to use the model case of benzoylacetone to investigate the problem whether or not the structure and/or dynamic behaviour of azo coupling products from enaminones are affected in the same way too. In the present paper we have studied the behaviour of both the possible types of enaminones (Scheme 1), which makes it possible to compare the effects of methyl and phenyl groups.

Results and discussion

Enaminones with primary amino group

Compounds **2–5** (Scheme 2) were prepared by azo coupling with enaminone **1a**, compounds **14, 15** (Scheme 3) by azo coupling with enaminone **1b**. On the basis of the results obtained from multinuclear magnetic resonance, compounds **2–5** in deuteriochloroform solutions have the structures shown in Scheme 2. The ^1H, ^{13}C, as well as ^{15}N NMR spectra (Tables 1–3) show a single set of signals only, which indicates that a tautomeric equilibrium, if present at all, should be rapid on the NMR time scale.



2 (X = NO_2); **3** (X = $N(CH_3)_2$); **4** (X = OCH_3); **5** (X = CH_3)

Scheme 2

The position of the azo-hydrazone tautomeric equilibrium, which is rapid on NMR time scale, can be best evaluated by means of weighted average of ^{15}N NMR parameters. For the azo and hydrazo forms the limiting values are approximately $\delta(^{15}N_\alpha) = 69.4$ and $\delta(^{15}N_\beta) = 126.9$, and $\delta(^{15}N_\alpha) = -205.2$ and $\delta(^{15}N_\beta) = -17.3$, respectively, and $^1J(^{15}N_\alpha, ^1H) = 0$ Hz and 95 Hz

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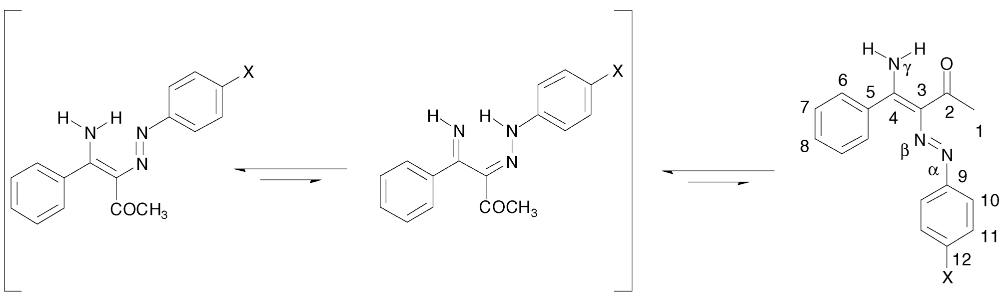


a **b**

14 (X = CH_3) **15** (X = H)

Scheme 3

Table 1 ^{15}N NMR parameters of the compounds **2–16**^{a} in $CDCl_3$

	N_α	N_β	N_γ	X	$^1J(^{15}N_\gamma, ^1H)$
2	−80.9	59.3	−178.8	−11.6	
3	22.6	91.8	−252.4	−332.4	
4	15.9	97.2	−246.7		
5	−15.0	^{c}	−231.7		
6	−196.2	−9.7	−70.0		4.9
7	−181.8	−2.2	−82.7		8.6
8	−210.1	−23.1	−56.9	−12.9	5.6
9	−199.6	−13.2	−68.6		4.2
10	−184.7	−4.1	−80.2		9.7
11	−164.7	5.8^b	−95.9	−336.2	17.2
12	−157.7	9.8	−111.7		16.8
13	−205.0	−20.0	−72.4	−12.4	88.8
14a	−78.9	49.7	−181.3		
^{15}N-**15a**	−106.8	36.4	^{c,d}		
^{15}N-**15b**	79.5	117.6	^{c,d}		
16a	−231.0	−35.0	^{c}		
16b	−211.3	−18.4	^{c}		
16c	−198.1	−13.5	^{c}		

^{a} For numbering see Scheme 2 (compds. **2–5**), Scheme 3 (compds. **14, 15**), Scheme 5 (compds. **6–13**) and Scheme 6 (comp. **16**). ^{b} $^2J(^{15}N_\beta, ^1H)$ = 2.2 Hz. ^{c} Not detected. ^{d} Two forms of double ^{15}N labelled compound ^{15}N-**15** (see Experimental)

respectively. Values of the ^{15}N NMR parameters of compounds **2–16** are in Table 1. The position of azo–hydrazone tautomeric equilibrium in deuteriochloroform solution was determined on the basis of ^{15}N NMR parameters of the individual compounds (Table 1).

The population of tautomers in compounds **2–5** is comparable with analogous derivatives of acetylacetone.[1,3,8] The content of hydrazone form increases in the order: 4-$N(CH_3)_2$ < 4-OCH_3 < 4-CH_3 < 4-NO_2; the 4-nitro derivative **2** is composed of 46% hydrazone and 54% azo form in $CDCl_3$ solution. At the same time, according to $\delta(^{15}N_\gamma)$, the double bond character of the C–N bond is increased in the same order (in 3-amino-1-fenylbut-2-en-1-one itself it is $\delta(NH_2)$ −281.9) (Table 1).

The products of azo coupling reactions with 4-amino-4-phenylbut-3-en-2-one **1b** were obtained in sufficient yields only when using benzenediazonium or 4-methylbenzenediazonium tetrafluoroborates. The reactions with 4-methoxy- and 4-(dimethylamino)benzenediazonium tetrafluoroborates proceeded very slowly, and the reaction mixture contained predominantly non-reacted enaminone even after 4 days.

In contrast to compounds **2–5**, substances **14, 15** exist in $CDCl_3$ solution as mixtures of two forms present in a ratio of 2 : 1 (according to integrals of NH protons of both forms) (Fig. 1). These forms are geometrical isomers *E* and *Z* differing in the

Table 2 ^{13}C chemical shifts of the compounds^a **2–5** and **14**^{b} in $CDCl_3$

	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10	C-11	C-12	X
2	193.20	131.74	166.75	26.13	139.50	130.03	118.42	131.43	144.76	127.56	125.10	153.00	
3	194.52	127.23	158.62	23.73	141.83	129.79	126.97	129.85	150.02	121.90	112.01	142.87	40.32
4	194.56	127.46	160.01	23.72	141.58	129.68	127.06	130.05	145.98	121.78	113.96	159.01	55.24
5	194.31	128.10	161.64	24.23	141.23	130.18	120.07	129.72	148.99	127.13	129.43	137.05	20.94
14a	26.88	196.80	130.27	163.96	129.21	126.26	128.24	127.67	145.57	129.72	118.26	136.18	20.95
14b	31.76	196.39	128.87	164.89	129.50	^{c}	^{c}	^{c}	151.11	129.34	121.29	138.01	20.95

^{a} For numbering see Scheme 2 (compds. **2–5**) and Scheme 3 (compd. **14**) ^{b} The spectrum of compound **15** is not presented because of strong broadening of the signals, which prevents interpretation of the spectrum and identification of some signals. ^{c} Not assigned due to strong overlapping of ^{1}H NMR signals.

Table 3 ^{1}H chemical shifts of the compounds^a **2–5** and **14,15** in $CDCl_3$

	H-4/H-1^b	H-6	H-7	H-8	H-10	H-11	NH_2^{c}	X
2	2.58 s	7.80 m	7.43 m	7.53 m	7.34 m	8.16 m	8.10 bs;14.45 bs	
3	2.52 s	7.70 m	7.35 m	7.41 m	7.30 m	6.54 m	6.54 m;12.87 bs	2.92 s
4	2.52 s	7.69 m	7.36 m	7.42 m	7.30 m	6.79 m	7.05 bs;12.98 bs	3.74 s
5	2.52 s	7.69 m	7.39 m	7.39 m	7.23 m	7.07 m	7.39 m;13.35 bs	2.28 s
14a	2.47 s	7.26 m	7.36 m	7.36 m	7.19 m	7.42 m	7.86 bs;13.59 bs	2.34 s
14b	2.55 s	7.36 m	7.36 m	7.36 m	7.07 m	7.19 m	5.84 bs;10.65 bs	2.28 s
15a	2.59 bs	^{d}	^{d}	^{d}	^{d}	^{d}	8.39 bs;13.88 bs	
15b	2.59 bs	^{d}	^{d}	^{d}	^{d}	^{d}	5.86 bs;10.82 bs	

^{a} For numbering see Scheme 2 (compds. **2–5**) and Scheme 3 (compds. **14,15**). ^{b} For compounds **14** and **15**. ^{c} Values of $^1J(^{15}N, ^1H)$: **2** 74.5 (8.10 ppm) and 45.9 (14.45 ppm); **4** 91.8 (7.05 ppm) and 84.2 (12.98 ppm); **5** 81.8 (7.39 ppm) and 67.6 (13.35 ppm); **14a** 71.7 (7.86 ppm) and 35.7 (13.59 ppm). ^{d} The signals of aromatic protons of both forms are strongly overlapping and together form two broad multiplets about 7.25 and 7.47 ppm.

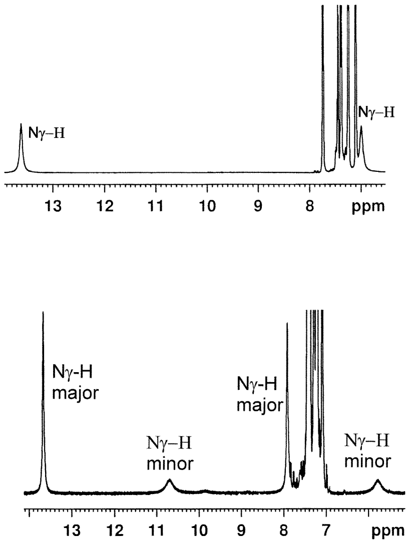


Fig. 1 Detail of 500 MHz proton NMR spectra of compounds **5** (upper part) and **14** (lower part) in $CDCl_3$.

type of intramolecular hydrogen bond. The differentiation as to which of the isomers is the major one and which the minor one was possible on the basis of different chemical shifts of methyl groups in CH_3CO groups in the carbonyl groups bonded or non-bonded by intramolecular hydrogen bond C=O · · · H–N (with pentane-2,3,4-trione 3-phenylhydrazone it is 31.44 or 26.39 ppm, respectively[9]). A comparison of these data with the chemical shifts observed with the major and the minor forms (Table 2) allows the conclusion that the *Z* isomer is predominant in this case (Scheme 3).

The azo–hydrazone tautomeric equilibrium of the major form is shifted somewhat more in the favour of the hydrazone form (as compared with analogous derivatives **2–5**); however, the azo form is still predominating (Scheme 3).

The nitrogen chemical shifts of the minor form of compound ^{15}N-**15** (117.6 and 79.5 ppm) indicate that this form in deuteriochlorform solution exists practically exclusively as the azo tautomer, like the minor form of the derivatives obtained from 4-aminopent-3-en-2-one.[1]

There exists a dynamic equilibrium between both isomers, which is caused by the partially decreased bond order of the polarised double bond, which was proved by means of H,H-EXSY (Fig. 2a,b). The proton exchange between NH groups of the major and the minor forms is only observable at the mixing time of 30 ms (Fig. 2b). Hence, the exchange between the major and the minor forms is somewhat faster than that in the case of analogous acetylacetone derivatives.[1] Chemical exchanges of protons of NH_2 groups inside each form are observable already at 5 ms (Fig. 2a). The chemical exchanges taking place are shown in Scheme 4. The ^{1}H, ^{13}C and ^{15}N NMR data of compounds **2–5, 14, 15** are given in Tables 1–3.

In the crystalline state, at 150 K both structures **3** and **14** consist of a mixture of the two tautomeric forms amino-diazenyl and imino-hydrazone in the ratio 85 : 15 and 82 : 18, respectively. The two compounds displays similar N1 · · · N3 hydrogen bond distances of 2.630(2) and 2.639(3) Å assisted by extended delocalization within the conjugated H_2N3–C2=C1–N2=N1 system (for numbering see Figs. 3a and 4a). The N1 · · · N3 hydrogen bond distances are quite longer than those, in the range 2.56–2.60 Å, observed in other four similar structures,[3,10,11] which, on the other hand, show unexpected lower delocalizations within the heterodienic moieties. These discrepancies can be interpreted considering that the structures **3** and **14** contain electron-donating *para* substituents, such as $N(CH_3)_2$ and CH_3 groups, while the other four structures contain electron-withdrawing substituents which seem to favour both the equalization of N1 and N3 proton affinities and the shortening of N1 · · · N3 hydro-

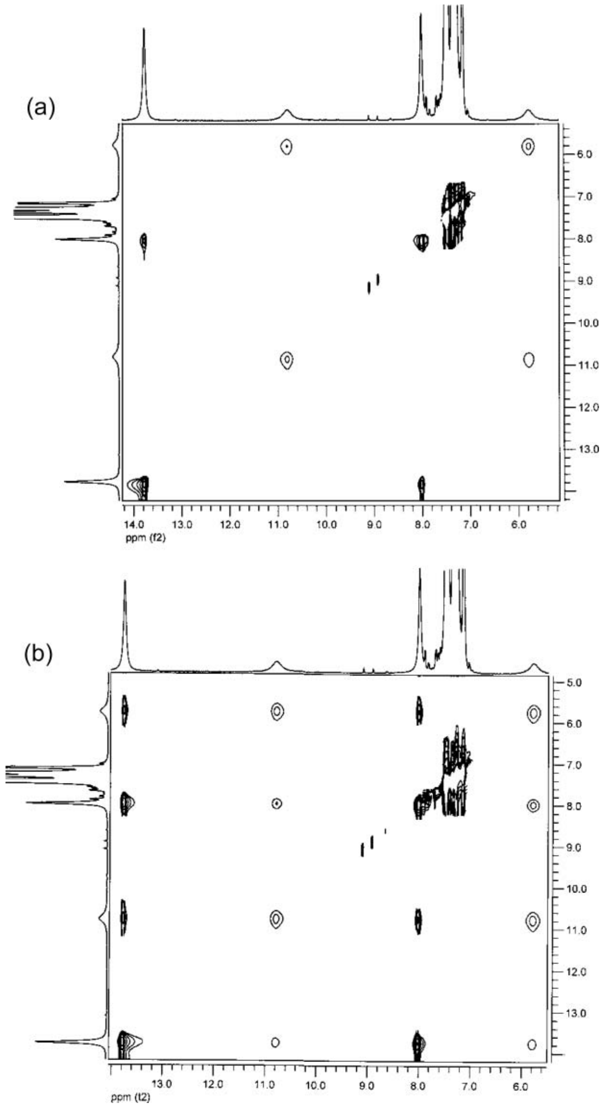


Fig. 2 (a) ^{1}H–^{1}H EXSY spectrum of **14** in $CDCl_3$, mixing time 5 ms. For assignments see Fig. 1. (b) ^{1}H–^{1}H EXSY spectrum of **14** in $CDCl_3$, mixing time 30 ms. For assignments see Fig. 1.

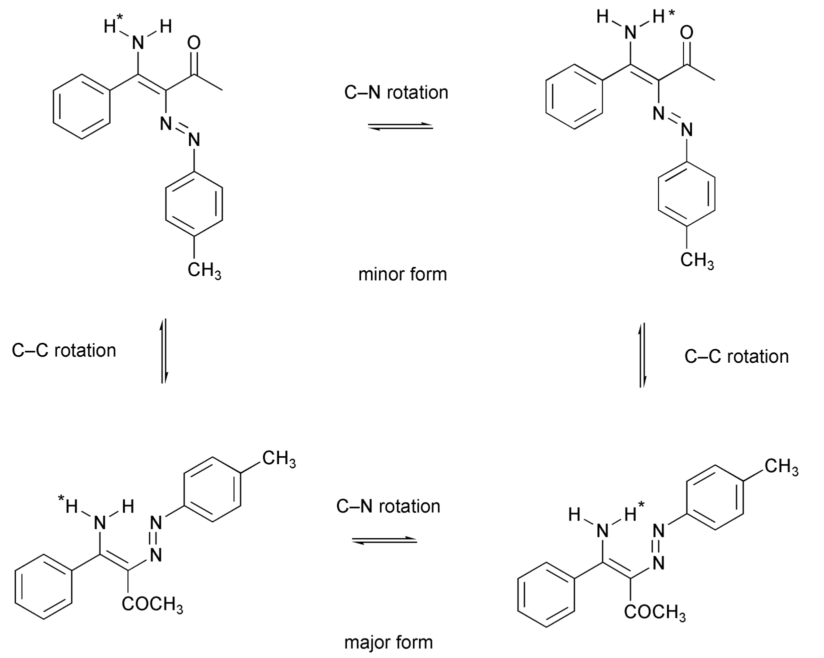
gen bond distances, but not the heterodienic delocalization. An opposite effect will be observed in compound **9** (Scheme 5) (*vide infra*) and in other systems, such as keto-arylhydrazones, where electron-withdrawing substituents on the arylhydrazone group tend to weaken the intramolecular N · · · O hydrogen bond.[12,13] These results suggest that in heterodienic asymmetric systems the intramolecular hydrogen bond shortening is determined by a combination of Resonant Assisted Hydrogen Bonding (RAHB) effects and proton affinity equalization of the atoms involved in intramolecular hydrogen bonds which is tuned by the electronic properties of substituents at the phenyl rings bonded to nitrogen atoms. RAHB[14] is a synergistic reinforcement of hydrogen-bond strength and delocalization of the π-conjugated chain connecting hydrogen-bond donor and acceptor atoms.

In both crystals of compounds **3** and **14** the molecules are linked in chains by means of N–H · · · O1 intermolecular hydrogen bonds as shown in Figs. 3b and 4b and in Table 4.

Enaminones with *N*-aryl group

The structure of azo coupling products obtained from enaminones type **1c–f** is expressed in Scheme 5.

The hydrazone form is strongly predominant in these compounds (75–90%), in contrast to compounds **2–5**. The position of this equilibrium is affected by substituents on the arylhydrazone group (the electron donor substituents increase the content



Scheme 4

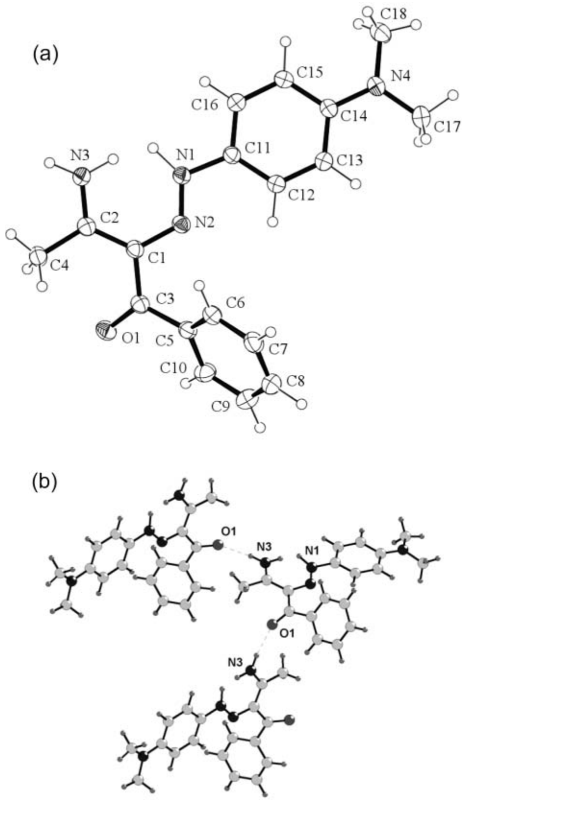


Fig. 3 (a) ORTEP view of compound **3** showing the thermal ellipsoids at 40% probability. Both tautomeric hydrogens, linked to N1 and N3 atoms, are displayed. (b) Chain of hydrogen bonded molecules in crystal packing of compound **3**.

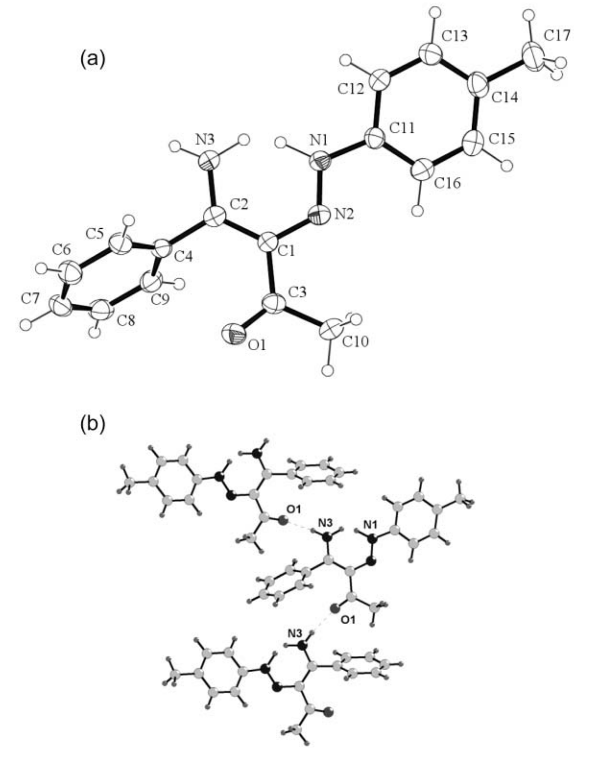
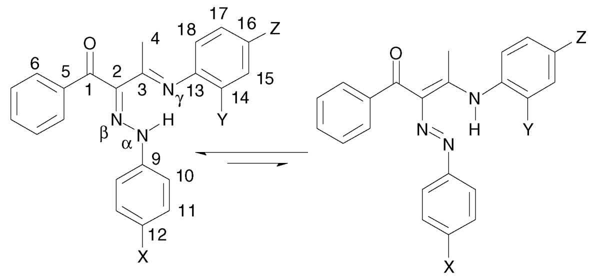


Fig. 4 (a) ORTEP view of compound **14** showing the thermal ellipsoids at 40% probability. Both tautomeric hydrogens, linked to N1 and N3 atoms, are displayed. (b) Chain of hydrogen bonded molecules in crystal packing of compound **14**.

of azo form). In the NMR spectra there only exists one set of signals corresponding to the tautomeric mixture of the azo and hydrazone forms with the latter strongly predominating. In this respect, these compounds strongly resemble analogous compounds derived from acetylacetone.[1] The nitrogen NMR parameters of compounds **6–13** are presented in Table 1; the ^{1}H and ^{13}C NMR parameters are given in Tables 5 and 6.

In the crystalline state, compound **9** displays (Fig. 5a) only the imino-hydrazone tautomeric form, too, where the imino and hydrazone groups are linked by an intramolecular N1–H · · · N3 short hydrogen bond assisted by resonance (RAHB)[14] with N1 · · · N3 distance of 2.611(2) Å. The heterodienic moiety N3=C2–C1=N2–N1H, involved in the intramolecular hydrogen bond formation, shows an extended π-conjugation where the delocalization within the H–N1–N2=C1 hydrazone group is greater than that observed for the N3=C2–C1 imino one owing to the contribution of resonance within the ketohydrazone moiety H–N1–N2=C1–C3=O1. In the strictly similar compound 4-(4-methoxyphenylamino)-3-phenylazo-3-penten-2-one,[2] in spite of comparable π-conjugation within the imino-hydrazone group,



6 (Y = Z = H, X = CH_3) **7** (Y = Z = H, X = OCH_3)
8 (Y = Z = H, X = NO_2) **9** (Y = Z = H, X = Br)
10 (Y= H, Z = OCH_3, X = CH_3 **11** (Y = H, Z = $N(CH_3)_2$, X = CH_3
12 (Y = Z = OCH_3, X = OCH_3) **13** (Y = Z = OCH_3, X = NO_2)

Scheme 5

there is a dramatic shortening of N1 · · · N3 hydrogen bond distance to 2.479(3) Å and a centering of the hydrogen atom in between the two nitrogens. These structural variations can be ascribed to the different electronic properties of *para*-substituents on the imino-phenyl group, a methoxy group instead of a bromine atom in compound **9**, showing that the *p*-OCH_3 group seems to better support the equalization of proton affinities of the two nitrogens involved in the intramolecular H-bond, rather than the *p*-Br substituent.

The crystal packing of compound **9** is dominated by chains of molecules linked by means of Br1 · · · O1 contacts of 3.099(1) Å, rather shorter than the sum of van der Waals radii of 3.37 Å (Fig. 5b). This interaction may be interpreted as a stabilizing intermolecular charge transfer complex with electron donation from the oxygen lone pair to the lowest unoccupied orbital on the C–Br bond, an interaction often studied by crystallographic methods.[15]

The proton NMR spectrum of compound **16** (Fig. 6) reveals the presence of three forms **16a,b,c** at a ratio of 10 : 2 : 1 (Fig. 6). The fact that there exists an equilibrium between these three forms was confirmed by finding the same population of the forms after recrystallisations from two different solvents (ethanol, cyclohexane). The presence of a hydrolysis product was excluded. The broadened proton signal of the major form ($\delta \sim 8$ ppm) denoted in Fig. 6 by a broken-line arrow undoubtedly belongs to the NH proton—see the detailed 1D ^1H–^{15}N HMBC in Fig. 7 with $^1J(^{15}N, ^1H) = 92.5$ Hz. The chemical shift of the nitrogen atom carrying this proton is −231 ppm (Fig. 8). These characteristics are typical of a hydrazone form without intramolecular hydrogen bonds.[16]

The structure of the major form was studied by means of NOE spectroscopy. The NOE interactions of NH proton are depicted in Scheme 6, and on the basis of them it was possible to suggest structure **16a** for the major form.

The remaining two forms **16b** and **16c** are hydrazones too, in accordance with the values of $^1J(^{15}N, ^1H)$ (Fig. 7) and $\delta(^{15}N)$ (Fig. 8); and judging by the chemical shifts of their NH protons (δ 14.93 and 14.09) there exist intramolecular hydrogen bonds N–H · · · N and N–H · · · O=C, respectively, in their molecules. On the basis of chemical shifts of $COCH_3$ groups in compounds **16a–c** (24.31, 28.14 and 26.26 ppm, respectively) it can be deduced that the **16b** form has its carbonyl group bonded by an intramolecular hydrogen bond and, hence, the **16c** form has an intramolecular hydrogen bond N–H · · · N. The NMR parameters of the individual forms of compounds **16** are presented in Tables 1, 5 and 6. Because of considerable overlapping it was impossible to assign or identify some signals in the ^1H and ^{13}C NMR spectra.

Hence, compound **16** differs considerably from analogous compounds **6–13** and analogous derivatives of acetylacetone. The preparation of a crystal suitable for X-ray diffraction study has been unsuccessful so far.

Conclusions

The position of tautomeric equilibrium is affected first of all by the type of amino group in the starting enaminone (azo form being predominant with a primary amino group, while hydrazone predominates with arylamino group), which is an identical situation with that of analogous derivatives of acetylacetone.

In the case of the substances studied, no significant changes in the position of the azo–hydrazone tautomeric equilibrium are caused by transition from $CDCl_3$ solution to solid phase.

When going from the enaminones of type **1a,c–f** to the enaminones of type **1b,g** (in $CDCl_3$ solutions), we can observe an increased trend for the formation of geometrical isomers with different types of hydrogen bonds.

Experimental

General

The melting points were measured on a hot-stage microscope and were not corrected. The elemental analyses were carried out on an automatic analyser FISONS EA 1108.

NMR methods

The NMR spectra were measured using the following spectrometers: Bruker AMX 360 (360.14 MHz for ^1H, 90.57 MHz for ^{13}C and 36.50 MHz for ^{15}N) and Bruker Avance 500 (500.13 MHz for ^1H, 125.77 MHz for ^{13}C and 50.69 MHz for ^{15}N) at laboratory temperature. Hexamethyldisiloxane was used as the internal standard for ^1H (δ 0.05 in $CDCl_3$). The ^{13}C NMR spectra were standardised by means of the middle signal of the solvent multiplet (δ 76.9). The ^{15}N NMR spectra were standardised by means of external neat nitromethane placed in a coaxial capillary (δ 0.0).

The proton signals were assigned with the help of H,H COSY pulse sequence.

The nitrogen chemical shifts were measured by both direct detection and indirect detection (gradient selected) ^1H–^{15}N HMBC and were processed in the magnitude mode. The gradient ratios were 70 : 30 : 50.1. Experiments were performed with the

Table 4 Hydrogen bond parameters (Å and degrees)

	D–H	H · · · A	D · · · A	D–H · · · A
3				
N3–H31 · · · N1	0.94(3)	1.86(3)	2.630(2)	137(2)
N1–H1 · · · N3	1.04(12)	2.02(16)	2.630(2)	114(9)
N3–H32 · · · O1 ($3/2 - x, y - 1/2, 3/2 - z$)	0.92(2)	1.99(2)	2.910(2)	172(2)
14				
N3–H31 · · · N1	0.96(4)	1.88(4)	2.639(3)	133(4)
N1–H1 · · · N3	1.07(16)	1.74(18)	2.639(3)	138(14)
N3–H32 · · · O1 ($x - 1/2, 1/2 - y, 1/2 + z$)	0.92(2)	1.99(2)	2.887(3)	167(2)
9				
N1–H1 · · · N3	0.88(2)	1.93(2)	2.611(2)	134(2)

Table 5 ^{1}H chemical shifts of the compounds **6–13**[a] and **16a–c**[a] in $CDCl_3$

	H-4/H-1[b]	H-6	H-7	H-8	H-10	H-11	H-14	H-15	H-16	H-17	H-18	NH[c]	X
6	2.25 s	7.94 m	7.43 m	7.51 m	7.03 m	7.03 m	6.90 m	7.38 m	7.15 m			15.66 bs	2.27 s
7	2.31 s	7.92 m	7.44 m	7.52 m	7.10 m	6.80 m	6.93 m	7.40 m	7.18 m			15.84 bs	3.75 s
8	2.22 s	7.99 m	7.48 m	7.60 m	7.14 m	8.09 m	6.92 m	7.41 m	7.20 m			15.54 bs	
9	2.26 s	7.94 m	7.46 m	7.55 m	7.00 m	7.34 m	6.91 m	7.40 m	7.18 m			15.60 bs	
10	2.25 s	7.93 m	7.43 m	7.51 m	7.04 m	7.04 m	6.93 m	6.88 m				15.88 bs	2.31 s (CH_3), 3.80 s (OCH_3)
11	2.38 s	7.91 m	7.42 m	7.50 m	7.06 m	7.06 m	6.92 m	6.77 m				16.15 bs	2.27 s (CH_3), 2.96 s ($N(CH_3)_2$)
12	2.38 s	7.90 m	7.42 m	7.50 m	7.16 m	6.81 m		6.57 d, $J_{H,H}$ 2.5		6.52 dd, $J_{H,H}$ 2.6, 8.5	6.92 d, $J_{H,H}$ 8.5	16.02 bs	3.75 s (OCH_3 12), 3.83 s (OCH_3 16), 3.87 s (OCH_3 14)
13	2.31 s	7.99 m	7.49 m	7.59 m	7.19 m	8.15 m		6.61 d, $J_{H,H}$ 2.5		6.54 dd, $J_{H,H}$ 2.6, 8.6	6.90 d, $J_{H,H}$ 8.5	15.89 bs	3.85 s (OCH_3 16), 3.91 s (OCH_3 14)
16a	2.35 s	6.85 m	7.19 m	7.03 m	6.92 m	7.05 m	7.78 m	7.41 m	7.46 m			8.03 bs	2.26 s
16b	1.92 s	[d]	[d]	[d]	[d]	[d]	7.95 m	7.43 m	[d]			14.09 bs	2.28 s
16c	2.46 s	6.66 m	7.13 m	6.98 m	7.27 m	7.16 m	[d]	[d]	[d]			14.93 bs	2.33 s

[a] For numbering see Scheme 5 (compds. **6–13**) and Scheme 6 (comp. **16**). [b] For compound **16**. [c] Values of $^{1}J(^{15}N_{\alpha}, ^{1}H)$: **6** 90.2; **7** 82.3; **8** 92.0; **9** 88.0; **10** 82.5; **11** 72.3; **12** 74.9; **13** 88.8; **16a** 92.5; **16b** 95.7; **16c** 90.4. [d] Not assigned due to overlapping by signals of **16a**.

Table 6 ^{13}C chemical shifts of the compounds **6–13**[a] and **16a–c**[a] in $CDCl_3$

	6	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**16a**	**16b**	**16c**
C-1	192.79	192.89	192.00	192.58	192.82	193.11	193.17	192.41	24.31	28.14	26.26
C-2	133.92	131.88	135.91	133.34	133.92	132.25	132.40	137.10	196.00	193.53	196.49
C-3	166.24	165.70	166.34	166.27	165.79	164.07	164.13	164.50	138.97	131.25	133.56
C-4	20.18	20.02	20.15	20.16	20.02	20.00	20.19	20.62	161.95	163.86	164.77
C-5	130.47	130.35	130.39	138.42	130.38	139.60	139.93	137.82	150.04	[b]	146.87
C-6	130.47	130.35	130.39	130.42	130.38	130.39	130.31	130.44	118.43	[b]	121.66
C-7	127.52	127.46	127.87	127.65	127.42	127.37	127.32	127.82	128.63	[b]	128.31
C-8	131.48	131.26	125.00	131.84	131.31	131.12	130.89	132.29	125.10	[b]	124.09
C-9	140.71	137.29	148.07	142.20	141.20	142.34	138.89	148.96	139.50	139.84	140.46
C-10	115.69	117.29	114.71	117.13	115.83	116.30	117.86	114.82	114.21	[b]	115.71
C-11	129.81	114.55	125.46	132.19	129.72	129.69	114.44	125.58	129.72	[b]	[b]
C-12	126.95	156.87	142.87	116.56	132.38	134.07	156.88	142.68	132.77	[b]	134.27
C-13	147.29	146.60	146.80	146.91	139.18	134.64	127.12	128.23	135.19	[b]	[b]
C-14	120.57	120.91	120.10	120.47	122.23	123.00	152.30	152.08	127.50	128.39	[b]
C-15	129.05	129.05	129.13	129.11	114.24	112.73	99.22	99.28	128.91	[b]	[b]
C-16	124.49	124.62	132.53	124.74	156.86	148.34	158.57	159.00	131.76	[b]	[b]
C-17							103.72	103.82			
C-18							122.88	121.94			
X	20.77	55.39			20.72 (CH_3), 55.33 (OCH_3)	20.77 (CH_3), 40.66 ($N(CH_3)_2$)	55.38(OCH_3 12), 55.47(OCH_3 16), 55.58(OCH_3 14)	55.50(OCH_3 16), 55.66(OCH_3 14)	20.56	20.70	20.80

[a] For numbering see Scheme 5 (compds. **6–13**) and Scheme 6 (comp. **16**). [b] Not assigned due to overlapping of proton NMR signals.

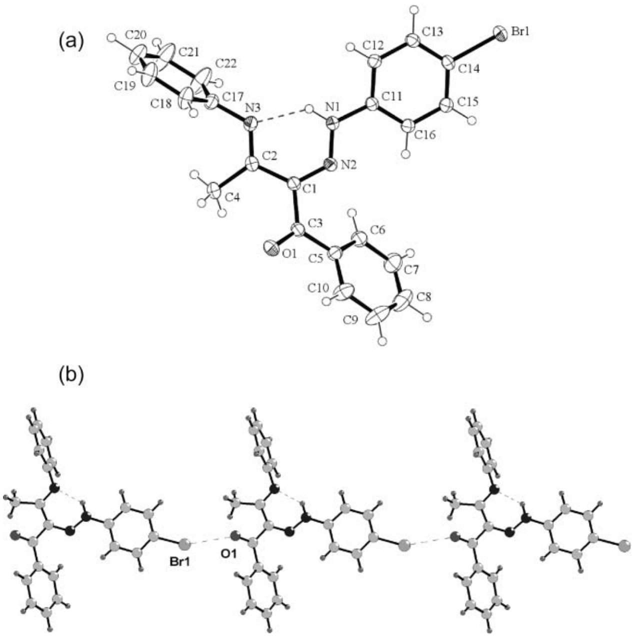


Fig. 5 (a) ORTEP view of compound **9** showing the thermal ellipsoids at 40% probability. (b) Chain of molecules linked by Br · · · O interactions in crystal packing of compound **9**.

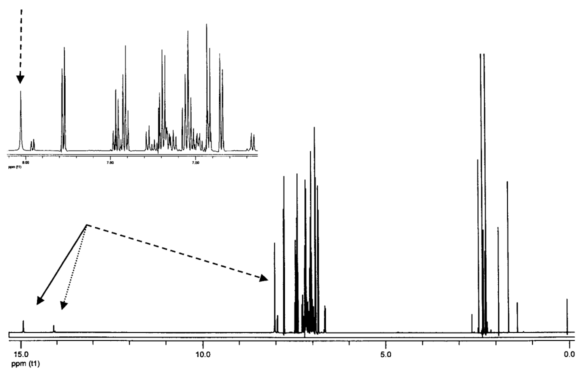


Fig. 6 500 MHz proton NMR spectrum of compound **16** in $CDCl_3$ together with the detail of the aromatic region. Arrows denote different NH protons belonging to individual forms.

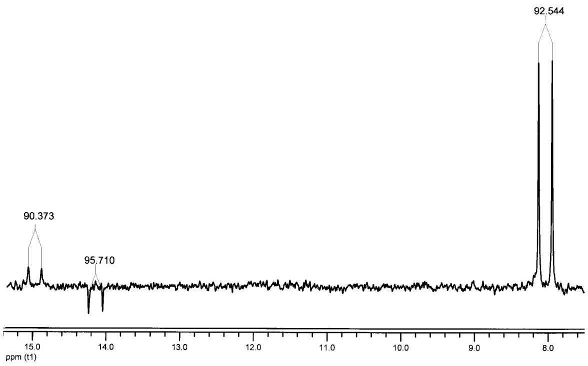


Fig. 7 500 MHz 1D *gs* ^1H–^{15}N HMBC spectrum of compound **16** in $CDCl_3$ optimised for 90 Hz.

NH one-bond coupling 90 Hz, and NH long-range coupling 5 Hz, 2k × 160 zero filled to 2k × 1k, sinebell squared in both dimensions. The values of coupling constants $J(^{15}N, ^1H)$ were read either from the ^{15}N INEPT spectra measured without proton decoupling or from the ^{15}N satellites in proton spectra or from 1D ^1H–^{15}N HMBC spectra.

The carbon NMR spectra were measured in the standard way and by means of the APT pulse sequence (spectral width

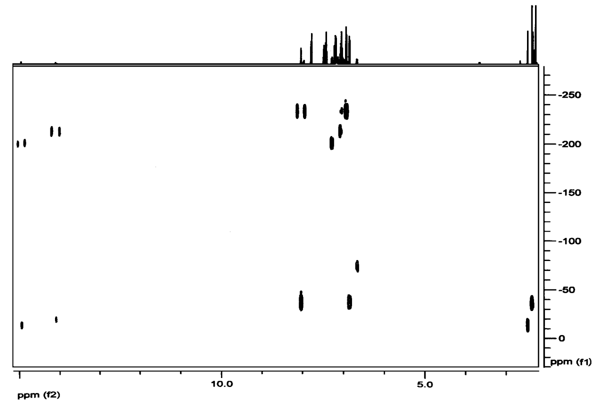


Fig. 8 500 MHz 2D *gs* ^1H–^{15}N HMBC spectrum of compound **16** in $CDCl_3$ optimised for 5 Hz.

26.455 kHz, acquisition time 1.238 s, zero filling to 64 K and line broadening 1 Hz prior to Fourier transformation). The assignment of the individual signals was carried out by means of 2D pulse sequences *gs* ^1H–^{13}C HMQC (experiment performed with the CH coupling 145 Hz, 2k × 128 zero filled to 2k × 1k, sinebell squared in both dimensions) and *gs* ^1H–^{13}C HMBC (experiment performed with the long-range CH coupling 6–10 Hz, 2k × 160 zero filled to 2k × 1k, sinebell squared in both dimensions) each processed in the magnitude mode.

The NOE experiments were carried out by means of the NOE difference spectra and by means of the 2D NOESY (mixing time 1.1 s, 2k × 128 zero filled to 2k × 1k, sinebell squared in both dimensions) processed in phase sensitive mode.

The 2D EXSY spectra were measured by means of the pulse sequence NOESY (mixing times 5, 30 and 100 ms, 2k × 128 zero filled to 2k × 1k, sinebell squared in both dimensions) supplied by Bruker Comp. The phasing was carried in a way giving the positive intensity for diagonal signals.

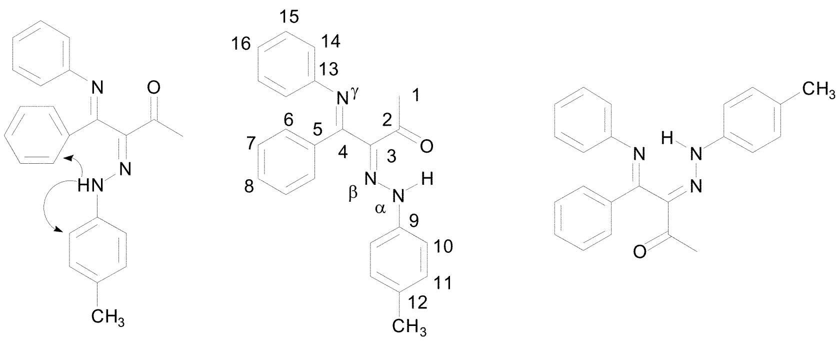
Crystallography

The crystal data for compounds **3, 9** and **14** were collected at $T = 150$ K using a Nonius Kappa CCD diffractometer with graphite monochromated Mo-Kα radiation and corrected for Lorentz, polarization effects. The data of compound **14** were corrected also for absorption effects (SORTAV).[17] The structures were solved by direct methods (SIR97)[18] and refined using full-matrix least-squares methods. All non-hydrogen atoms were refined anisotropically and hydrogens isotropically. In structures **3** and **14** the difference Fourier showed diffuse electron density between N1 and N3 atoms with two maxima from which two proton positions could be identified. Refinement of the two tautomeric H atoms with partial occupancy and isotropic thermal parameters fixed at 1.2 times the average of those of the nitrogen atoms was successfully attempted giving the final occupancy factors of 85% for H31 and 15% for H1, and 82% for H31 and 18% for H1 in structures **3** and **14**, respectively. Furthermore, the crystal of compound **3** contains also molecules of solvent toluene disordered around centres of symmetry. All the calculations were performed using SHELXL-97 (ref. 19) and PARST (ref. 20) implemented in the WINGX (ref. 21) system of programs. The crystal data and refinement parameters are summarized in Table 7. Selected interatomic distances and angles are given in Table 8.

CCDC reference numbers 259869–259871. See http://www.rsc.org/suppdata/ob/b5/b500173k/ for crystallographic data in .cif or other electronic format.

Materials

Dichloromethane was pre-dried by standing over anhydrous calcium chloride and by distillation over phosphorus pentoxide.



Scheme 6

Table 7 Crystal data

	3	14	9
Formula	$C_{18}H_{20}N_4O{\cdot}1/2(C_7H_8)$	$C_{17}H_{17}N_3O$	$C_{22}H_{18}BrN_3O$
M	354.45	279.34	420.30
System	Monoclinic	Monoclinic	Triclinic
Space group	$C2/c$	$P2_1/n$	$P\bar{1}$
a/Å	25.8225(3)	5.7502(1)	9.3969(3)
b/Å	10.7493(2)	29.8733(11)	10.5034(3)
c/Å	15.6270(1)	9.1184(3)	10.5516(4)
α/°	90	90	71.075(1)
β/°	117.694(1)	101.110(2)	88.902(2)
γ/°	90	90	81.541(1)
U/Å^3	3480.7(1)	1536.98(8)	973.97(6)
Z	8	4	2
D_c/g cm^{-3}	1.226	1.207	1.433
T/K	150	150	150
μ/cm^{-1}	0.78	0.77	21.26
θ_{min}–θ_{max}/°	3.6–28.0	3.1–27.5	3.4–30.0
Unique reflns	4585	3481	5579
R_{int}	0.028	0.056	0.034
Observed reflns [$I > 2\sigma(I)$]	4083	1828	5075
R (Obs. reflns)	0.0519	0.0587	0.0342
wR (All reflns)	0.1259	0.1347	0.0850
S	1.147	1.031	1.086
$\Delta\rho_{max}$; $\Delta\rho_{min}$/e Å^{-3}	0.21; −0.18	0.20; −0.23	0.35; −0.75

Table 8 Selected bond distances (Å), angles (°) and short contact distances (Å)

	3	14	9
Bond distances			
N1–N2	1.283(2)	1.283(3)	1.322(2)
C1–N2	1.385(2)	1.383(3)	1.314(2)
C1–C2	1.408(2)	1.408(3)	1.484(2)
C2–N3	1.325(2)	1.331(3)	1.285(2)
C1–C3	1.462(2)	1.472(3)	1.490(2)
C3–O1	1.241(2)	1.227(3)	1.226(2)
N1–C11	1.422(2)	1.427(3)	1.403(2)
N3–C17			1.433(2)
Bond angles			
C11–N1–N2	113.0(1)	113.2(2)	118.9(1)
N1–N2–C1	119.2(1)	118.8(2)	120.8(1)
N2–C1–C2	126.1(1)	125.5(2)	126.5(2)
N2–C1–C3	113.2(1)	112.8(2)	112.8(2)
C2–C1–C3	120.7(1)	121.6(2)	120.6(1)
C1–C2–N3	120.7(1)	121.8(2)	117.1(2)
C1–C2–C4	123.0(1)	123.1(2)	118.9(2)
N3–C2–C4	116.2(2)	115.1(2)	123.8(2)
C1–C3–O1	122.3(1)	122.7(2)	119.2(2)
C1–C3–C5	119.6(1)		121.0(1)
C1–C3–C10		118.2(2)	
C2–N3–C17			120.6(2)

Anhydrous sodium acetate was re-melted on a porcelain dish and left to cool in a desiccator.

The diazonium tetrafluoroborates were prepared by a known procedure.[6]

Acetanhydride was distilled over phosphorus pentoxide immediately prior to its use.

3-Amino-1-phenylbut-2-en-1-one 1a. Benzoylacetone (0.05 mol) was heated with 100 ml 25% aqueous ammonia (1.34 mol) to boiling for 5 h. The product separated by cooling was collected by suction and recrystallized from toluene. Yield 52%; mp 141–143 °C (lit.[22] 144–145 °C).

δ_H (500 MHz, $CDCl_3$) 2.00 (3H, s, CH_3), 5.50 (1H, bs, NH), 5.70 (1H, bs, NH), 7.39 (3H, m, Ar), 7.84 (2H, m, Ar), 10.18 (1H, bs, NH); δ_C (125 MHz, $CDCl_3$) 22.60 (CH_3), 92.03 (=C–H), 126.88, 128.02, 130.60 (3 × CH Ar), 140.05 (C_q Ar), 163.06 (=C–N), 189.20 (C=O); δ_N (50.69 MHz) −281.9.

4-Amino-4-phenylbut-3-en-2-one 1b. 5-Methyl-3-phenylisoxazol-4-carboxylic acid (0.05 mol) was hydrogenated under atmospheric pressure in ethyl acetate under catalysis of Raney nickel (RaNi) overnight. Catalyst was removed by suction, washed by a small amount of ethyl acetate and the filtrate was evaporated *in vacuo*. Residue was solidified by cooling. Crystallisation from cyclohexane. Yield 80%; mp 84–87 °C (lit.[23] 85–88 °C).

δ_H (500 MHz, $CDCl_3$) 2.15 (3H, s, CH_3), 5.23 (1H, bs, NH), 5.45 (1H, s, =CH), 7.44 (3H, m, Ar), 7.54 (2H, m, Ar), 9.94 (1H, bs, NH); δ_C (125 MHz, $CDCl_3$) 29.43 (CH_3), 94.72 (=C–H), 126.02, 128.59, 130.26 (3 × CH Ar), 136.81 (C_q Ar), 160.96 (=C–N), 197.11 (C=O); δ_N (50.69 MHz, $CDCl_3$) −292.2.

3-Phenylamino-1-phenylbut-2-en-1-one 1c. This compound was prepared according to the method described in ref. 24. Yield 85%; mp 107–108.5 °C (lit.[24] 110.5–111.5 °C).

δ_H (360.14 MHz, $CDCl_3$) 2.10 (3H, s, CH_3), 5.87 (1H, s, =CH), 7.14 (2H, m, Ar), 7.20 (1H, m, Ar), 7.33 (2H, m, Ar), 7.40 (3H, m, Ar), 7.90 (2H, m, Ar), 13.09 (1H, bs, NH); δ_C (90.57 MHz) 20.21 (CH_3), 94.45 (=CH), 124.55 (CH Ar), 125.57 (CH Ar), 126.87 (CH Ar), 128.08 (CH Ar), 128.97 (CH Ar), 130.70 (CH Ar), 138.46 (Cq Ar), 139.84 (Cq Ar), 162.00 (=C–N), 188.47 (C=O); δ_N (36.50 MHz, $CDCl_3$) −253.3.

3-(4-Methoxyphenylamino)-1-phenylbut-2-en-1-one 1d. This compound was prepared by the same method as **1c**. Crystallisation from toluene, yield 77%; mp 106–107 °C. (Found C 76.34; H 6.60; N 5.47. $C_{17}H_{17}NO_2$ requires C 76.38; H 6.41; N 5.24%).

δ_H (360.14 MHz, $CDCl_3$) 2.00 (3H, s, CH_3), 3.73 (3H, s, OCH_3), 5.83 (1H, s, =CH), 6.83 (2H, m, Ar), 7.05 (2H, m, Ar), 7.39 (3H, m, Ar), 7.89 (2H, m, Ar), 12.94 (1H, bs, NH); δ_C (90.57 MHz, $CDCl_3$) 19.89 (CH_3), 55.11 (OCH_3), 93.42 (=CH), 114.02 (CH Ar), 126.19 (CH Ar), 126.72 (CH Ar), 127.95 (CH Ar), 130.46 (CH Ar), 131.08 (C_q Ar), 139.82 (C_q Ar), 157.51 (C_q Ar), 162.81 (=C–N), 187.47 (C=O); δ_N (36.50 MHz, $CDCl_3$) −254.8.

3-(4-Dimethylaminophenylamino)-1-phenylbut-2-en-1-one 1e. This compound was prepared by the same method as **1c**. Crystallisation from toluene, yield 90%; mp 134.5–136.5 °C. (Found C 77.04; H 7.14; N 9.99. $C_{18}H_{20}N_2O$ requires C 77.11; H 7.19; N 9.99%).

δ_H (500.13 MHz, $CDCl_3$) 2.04 (3H, s, CH_3), 2.93 (6H, s, $N(CH_3)_2$), 5.81 (1H, s, =CH), 6.67 (2H, m, Ar), 7.03 (2H, m, Ar), 7.41 (3H, m, Ar), 7.89 (2H, m, Ar), 12.88 (1H, bs, NH); δ_C (125.77 MHz, $CDCl_3$) 20.09 (CH_3), 40.45 ($N(CH_3)_2$), 92.98 (=CH), 112.39 (CH Ar), 126.11 (CH Ar), 126.81 (CH Ar), 127.41 (C_q Ar), 128.04 (CH Ar), 130.41 (CH Ar), 140.18 (C_q Ar), 148.45 (C_q Ar), 163.45 (=C–N), 187.79 (C=O).

3-(2,4-Dimethoxyphenylamino)-1-phenylbut-2-en-1-one 1f. This compound was prepared according to the procedure described in ref. 25; the mp was in accordance with the literature value.[25]

4-Phenylbut-3-yn-2-one. A 500-ml three-necked flask was charged with phenylacetylene (0.1 mol) and 100 ml dry ether. Sodium metal (0.1 mol) was added to this solution with stirring. The mixture was stirred at room temperature overnight. Then the reaction mixture was diluted with another 100 ml ether. The suspension of sodium phenylacetylide was added portionwise through a silicone tube into a cooled solution of acetanhydride (0.1 mol) in 100 ml ether. The total time of addition of sodium phenylacetylide was 90 min. The mixture was stirred with cooling for another 5 h, and then without cooling overnight. With stirring, the reaction mixture was treated with 100 ml cold HCl (1 : 3), and when all the solid matter dissolved, the organic layer was separated, washed with 3 × 50 ml saturated Na_2CO_3 solution, and dried with anhydrous sodium sulfate. The solvent was evaporated in vacuum, and the evaporation residue was fractionated. The product boils at 93 °C/23 mbar. Ref. 26 gives bp 120–125 °C/14 Torr. Yield 37%.

4-Phenylamino-4-phenylbut-3-en-2-one 1g. This compound was prepared by reaction of 4-phenylbut-3-yn-2-one with aniline in ethanol according to the procedure described in ref. 27 Yield 55%, bp 178 °C/3 mbar (lit.[28] gives 175–178 °C/3 Torr.)

δ_H (360.13 MHz, $CDCl_3$) 2.41 (3H, c, $COCH_3$), 7.35 (2H, m, Ar), 7.42 (1H, m, Ar), 7.54 (2H, m, Ar).

General procedure of azo coupling reactions

Re-melted sodium acetate (15 mmol) and the respective benzenediazonium tetrafluoroborate were added to a solution of enaminone (5 mmol) in 30 ml dichloromethane with stirring. The reaction mixture was stirred at room temperature overnight (or for 4 days, in the case of compound **3**), whereupon the solids were collected by suction on a sintered-glass filter and the filter cake was washed with a small amount of dichloromethane. The filtrate was evaporated in vacuum, and the evaporation residue was either recrystallized or submitted to column chromatography. The following compounds were prepared by the procedure described.

3-Amino-2-(4-nitrophenyldiazenyl)-1-phenylbut-2-en-1-one 2. Crystallisation from toluene, yield 51%; mp 188–191 °C (Found C 62.14; H 4.57; N 17.95. $C_{16}H_{14}N_4O_3$ requires C 61.93; H 4.55; N 18.05%).

3-Amino-2-(4-dimethylaminophenyldiazenyl)-1-phenylbut-2-en-1-one 3. Crystallisation from toluene, yield 45%; mp 160–163 °C (Found C 70.18; H 6.54; N 18.09. $C_{18}H_{20}N_4O$ requires C 70.11; H 6.54; N 18.17%).

3-Amino-2-(4-methoxyphenyldiazenyl)-1-phenylbut-2-en-1-one 4. Crystallisation from a toluene–cyclohexane mixture, yield 51%; mp 129–132 °C (Found C 69.38; H 5.82; N 14.20. $C_{17}H_{17}N_3O_2$ requires C 69.14; H 5.80; N 14.23%).

3-Amino-2-(4-methylphenyldiazenyl)-1-phenylbut-2-en-1-one 5. Column chromatography on silica using a chloroform–ethyl acetate 3 : 2 mixture as eluent; crystallization from a toluene–cyclohexane mixture, yield 30%; mp 158–161 °C (Found C 73.08; H 6.22; N 14.85. $C_{17}H_{17}N_3O$ requires C 73.10; H 6.13; N 15.04%).

1-Phenyl-3-phenyliminobutane-1,2-dione 2-(4-methylphenylhydrazone) 6. Crystallisation from methanol, yield 31%; mp 133–136 °C (Found C 77.54; H 6.04; N 12.07. $C_{23}H_{21}N_3O$ requires C 77.72; H 5.96; N 11.82%).

1-Phenyl-3-phenyliminobutane-1,2-dione 2-(4-methoxyphenylhydrazone) 7. Crystallisation from ethanol, yield 57%; mp 122–124 °C (Found C 74.49; H 5.77; N 11.19. $C_{23}H_{21}N_3O_2$ requires C 74.37; H 5.70; N 11.31%).

1-Phenyl-3-phenyliminobutane-1,2-dione 2-(4-nitrophenylhydrazone) 8. Crystallisation from ethanol, yield 60%; mp 148–150 °C (Found C 68.20; H 4.66; N 14.26. $C_{22}H_{18}N_4O_3$ requires C 68.38; H 4.70; N 14.50%).

1-Phenyl-3-phenyliminobutane-1,2-dione 2-(4-bromophenylhydrazone) 9. Crystallisation from cyclohexane, yield 55%; mp 138–140 °C (Found C 63.01; H 4.30; N 10.11. $C_{22}H_{18}BrN_3O$ requires C 62.87; H 4.32; N 10.00%).

1-Phenyl-3-(4-methoxyphenylimino)butane-1,2-dione 2-(4-methylphenylhydrazone) 10. Crystallisation from ethanol, yield 98%; mp 151–153 °C (Found C 74.80, H 6.12; N 10.69. $C_{24}H_{23}N_3O_2$ requires C 74.78; H 6.01; N 10.90%).

1-Phenyl-3-(4-dimethylaminophenylimino)butane-1,2-dione 2-(4-methylphenylhydrazone) 11. Crystallisation from cyclohexane, yield 52%; mp 143.5–145 °C (Found C 75.56; H 6.66; N 14.00. $C_{25}H_{26}N_4O$ requires C 75.35; H 6.58; N 14.06%).

1-Phenyl-3-(2,4-dimethoxyphenylimino)butane-1,2-dione 2-(4-methoxyphenylhydrazone) 12. Crystallisation from ethanol, yield 56%; mp 122–125 °C (Found C 69.72; H 5.74; N 9.82. $C_{25}H_{25}N_3O_4$ requires C 69.59; H 5.84; N 9.74%).

1-Phenyl-3-(2,4-dimethoxyphenylimino)butane-1,2-dione 2-(4-nitrophenylhydrazone) 13. Crystallisation from an ethanol–chloroform mixture, yield 84%; mp 205–206.5 °C (Found C 64.30; H 4.71; N 12.38. $C_{24}H_{22}N_4O_5$ requires C 64.57; H 4.97; N 12.55%).

4-Amino-3-(4-methylphenyldiazenyl)-4-phenylbut-3-en-2-one 14. Column chromatography on silica using a chloroform–ethyl acetate 3 : 1 mixture as eluent; crystallisation from cyclohexane, yield 43%; mp 171.5–173 °C (Found C 73.25; H 6.26; N 15.10. $C_{17}H_{17}N_3O$ requires C 73.10; H 6.13; N 15.04%).

4-Amino-3-phenyldiazenyl-4-phenylbut-3-en-2-one 15. Column chromatography on silica using a *n*-hexane–ethyl acetate 1 : 1 mixture as eluent; crystallization from cyclohexane, yield 68%; mp 164–169 °C (Found C 72.56; H 5.76; N 15.93 $C_{16}H_{15}N_3O$ requires C 72.43; H 5.70; N 15.84%).

4-Amino-3-phenyldiazenyl-4-phenylbut-3-en-2-one 2 × ^{15}N labelled ^{15}N-15. This compound was prepared in the same way as **3b** isotopomer by using of double ^{15}N labelled benzenediazonium tetrafluoroborate (95% ^{15}N aniline, 55.5% ^{15}N sodium nitrite).

Yield 46%, mp 166–168 °C.

3-(4-Methylphenyldiazenyl)-4-phenylamino-4-phenylbut-3-en-2-one 16. Crystallisation from ethanol, yield 15% (after double crystallisation); mp 135–138 °C (Found C 77.71; H 6.08; N 11.69. $C_{23}H_{21}N_3O$ requires C 77.72; H 5.96; N 11.82%).

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