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Structure and tautomerism of azo coupling products from *N*-alkylenaminones derived from acetylacetone and benzoylacetone in solid phase and in solution†‡

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A series of azo coupling products have been prepared by reaction of substituted benzenediazonium tetrafluoroborates with *N*-alkyl 4-aminopent-3-en-2-ones or 3-amino-1-phenylbut-2-en-1-ones. The structure and tautomerism of the reaction products were studied by means of single-crystal X-ray study and by NMR spectroscopy in deuteriochloroform solution. The azo coupling products obtained from 4-methylaminopent-3-en-2-ones (**3a–i**) exist in $CDCl_3$ solution as *E*/*Z* isomer mixtures with the *Z* isomer strongly predominating. The major isomer is a mixture of enamino–azo and imino–hydrazo tautomers with the former predominating. The proportion of the azo form depends on substitution of the benzene ring of the diazonium salt and decreases in the order of MeO > Me > Br > NO_2. The position of tautomeric equilibrium is practically unaffected by switching from 4-methylaminopent-3-en-2-ones to 3-methylamino-1-phenylbut-2-en-1-ones. In the solid phase, the azo form always predominates; substitution of diazonium salt and at N3 nitrogen does not significantly affect the position of the tautomeric equilibrium. The azo coupling products always exist in the form of a single *Z* isomer. All determined structures, in the solid state, consist of a mixture of the two tautomeric forms, amino–diazenyl and imino–hydrazone, in ratios ranging from 82/18 to 91/9%. The weighed superimposition of both the hydrogen-bonded N1═N2–C1═C2–N3H/ HN1–N2═C1–C2═N3 heterodienic fragments, however, do not allow to clarify the effects of the *para*-substituents at the N1-phenyl ring both on the N1···N3 hydrogen-bond distances and on the bond lengths in the heterodienic systems within the series **3a–c,f** and **4a–c,e,f**.

Introduction

Enaminones are compounds widely used in organic synthesis, above all as precursors in syntheses of heterocyclic compounds.[1,2] They react easily with diazonium salts.[3] The products obtained are rewarding subjects of structural studies because of several potential tautomeric systems present in a single molecule (Scheme 1). Our previous papers dealt with the study of structure and tautomerism of azo coupling products obtained from several types of enaminones.[4–7a] Azo coupling reactions involving enaminones were also studied by the group of Elnagdi.[7b–d] Due to hydrolysis, however, only the products of azo coupling with 1,3-dicarbonyl compounds were isolated.

In the case of enaminones derived from acetylacetone we found[3,4] that substitution of the proton on the nitrogen by an aryl group causes a very distinct shift in tautomeric equilibrium in favour of the hydrazone form, the substitution of diazonium salt having virtually no effect upon the position of tautomeric equilibrium.[4] Transition to the solid phase did not cause any significant shift in the position of the azo–hydrazone tautomeric equilibrium.[8] On the other hand, if this enaminone possesses a primary amino group, then the position of tautomeric equilibrium shifts in favour of the azo form.[4] The position of tautomeric equilibrium in this case somewhat depended on the substitution of diazonium salt. Electron-acceptor substituents caused a stronger increase in proportion of hydrazone form than electron-donors did.[4,6] Transition from deuteriochloroform solution to the solid phase brought about a certain shift of tautomeric equilibrium in favour of the azo form, and the effect of substituents was virtually negligible.[6] Another difference between the solid phase and deuteriochloroform solution was in the fact that in solution the azo coupling product from 4-aminopent-3-en-2-one represented a mixture of *E* and *Z* isomers differing in the type of intramolecular hydrogen bond. The predominant *Z* isomer forms an intramolecular hydrogen bond of N–H···N type between nitrogen atoms of amino group and azo group, while the

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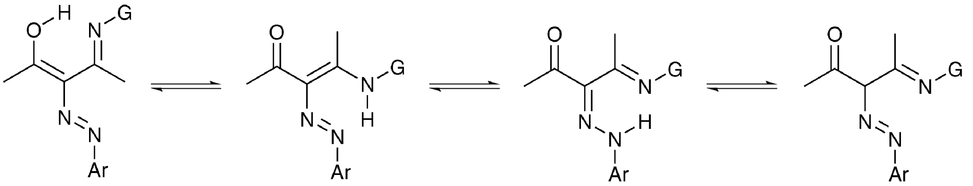


Scheme 1

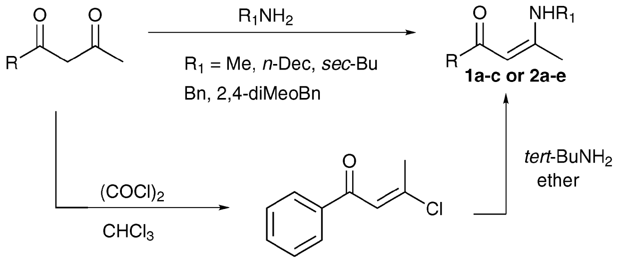
minor isomer *E* forms the intramolecular hydrogen bond of C=O···H–N type between the oxygen atom of carbonyl group and the proton on the nitrogen atom of the amino group.[4] In the solid phase the presence of isomer *Z* was only observed.[6] The other hydrogen atom of the amino group takes part in an intermolecular hydrogen bond of N–H···O=C type with an oxygen atom of a carbonyl group of a neighbouring molecule.[6] The effect of the introduction of a methyl group on the amino group of 4-aminopent-3-en-2-one has so far been studied only on the azo coupling product of benzenediazonium salt and 4-methylaminopent-3-en-2-one.[4] The results clearly showed that the given compound in $CDCl_3$ solution resembles the derivative with the primary amino group, *i.e.* its azo form is predominating even though its proportion is somewhat lower as compared with that in the derivative with a primary amino group. Again the compound exists in the form of a mixture of *E* and *Z* isomers. However, the substituent effect upon the position of tautomeric equilibrium was not studied in the case of these compounds, and neither was their structure in the solid phase. The aim of this work is to describe the structure of products obtained from substituted benzenediazonium tetrafluoroborates and 4-alkylaminopent-3-en-2-ones or 3-amino-1-phenylbut-2-en-1-ones depending on the type of enaminone, substitution of diazonium salt, and *N*-alkyl group of the enaminone.

Results and discussion

Synthesis of the starting enaminones and the azo coupling products

The starting enaminones, except for **2d**, were synthesised by reaction of the respective β-dicarbonyl compound with primary amines. In the case of **2d** this direct method failed, and the substance was prepared *via* the more reactive 3-chloro-1-phenylbut-2-en-1-one (Scheme 2).

The azo coupling products were prepared by reaction of the β-enaminone with the corresponding benzenediazonium tetrafluoroborate in the presence of sodium acetate. The solvent used in the case of acetylacetone derivatives was diisopropyl ether (except for **3g** and **3h**, in which case dichloromethane was used). Due to insolubility of benzoyl acetone derivatives in diisopropyl ether we also used dichloromethane in these cases.

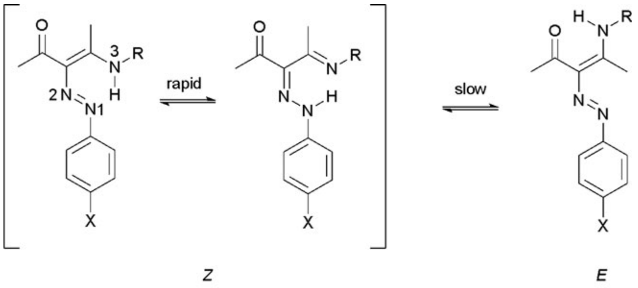


1a: R = Me, R_1 = Me **1b:** R = Me, R_1 = Bn
1c: R = Me, R_1 = 2,4-diMeOBn
2a: R = Ph, R_1 = Me **2b:** R = Ph, R_1 = 2,4-diMeOBn
2c: R = Ph, R_1 = *sec*-Bu **2d:** R = Ph, R_1 = *tert*-Bu
2e: R = Ph, R_1 = *n*-Dec

Scheme 2

Structure of azo coupling products in deuteriochloroform solution

The reaction products from substituted benzenediazonium tetrafluoroborates and 4-methylaminopent-3-en-2-one exist in deuteriochloroform solution as mixtures of *E* and *Z* isomers (Scheme 3). The proportion of isomers in products **3a,c,d** varied from 1 : 9 to 1 : 16, while in the case of nitro derivative **3b**, only one isomer was observed in $CDCl_3$ solution. The major form *Z* is a mixture of azo and hydrazone tautomers, the content of azo form being decreased by substituents at the 4-position of the diazonium ion in the order of $OCH_3 > CH_3 > Br > NO_2$. Only limited amount of NMR data could be obtained about the minor form (the chemical shifts of NH proton and N3 nitrogen—for numbering of nitrogen atoms see Schemes 3 and 4). The $\delta(^{15}NCH_3)$ values of the minor form of azo coupling products **3a** and **3c** are close to $\delta(^{15}N)$ of the starting enaminone **1a** (–280.6 ppm).[4] The enaminones derived from acetylacetone in $CDCl_3$ solution exist practically exclusively in their enamino form,[9] wherefrom it can be deduced that the minor form of azo coupling product possesses an enamino–azo arrangement in $CDCl_3$ solution. Comparison of



3a: R = Me, X = Me **3f:** R = Bn, X = H
3b: R = Me, X = NO_2 **3g:** R = Bn, X = Br
3c: R = Me, X = OMe **3h:** R = Bn, X = OMe
3d: R = Me, X = Br **3i:** R = 2,4-diMeOBn, X = OMe
3e: R = Bn, X = Me

Scheme 3

Table 1 ^1H NMR spectra of the compounds **3a–i** in $CDCl_3$

	H-1	H-5	H-7	H-8	H-9	NR	X	NH
3a	2.39 s	2.30 s	7.29–7.31 br m	7.02–7.03 m		2.83 br s	2.21 s	14.64 br s 12.06 br s
3b	2.51 s	2.52 s	7.51–7.55 m	8.18–8.22 m		3.24 s		15.21 br s
3c	2.54 s	2.52 s	7.51–7.53 br m	6.89–6.94 m		3.09 s	3.82 s	14.58 br s
3d	2.52 s	2.50 s	7.46–7.48 m	7.38–7.40 m		3.12 br s		14.85 br s 12.31 br s
3e	2.51 s	2.50 s	7.19–7.21 m	7.09–7.10 m		[a]	2.29 s	15.57 br s 12.61 br s
3f	2.50 s	2.47 s	7.27–7.38 br m		7.04–7.12 m	[b]		15.65 br s 12.64 br s
3g	2.61 s	2.58 s	7.35–7.44 br m		6.91–6.92 br m	[c]	3.83 s	15.32 br s 12.64 br s
3h	2.56 s	2.59 s	7.37–7.45 br m		7.20–7.21 br m	[d]		15.61 br s 12.78 br s
3i	2.60 s	2.51 s	7.35–7.40 br m	6.81–6.91 m		[e]	3.79 s	14.92 br s 12.46 br s

[a] NBn group: 4.58 br d 2H J = 2.23 Hz; 7.30–7.32 m 3H; 7.35–7.38 m 2H. [b] NBn group: 4.56 br s 2H, 7.27–7.38 m, 5H. [c] NBn group: 4.68 s 2H, 7.37–7.45 m 5H. [d] NBn group: 4.63 br s 2H, 7.35–7.44 br m 5H. [e] 2,4-diMeOBn group: 3.80 s 6H, 4.51 br s 2H, 6.45–6.48 m 2H, 7.12 d 1H J = 8.2 Hz.

Table 2 ^{13}C chemical shifts of the compounds **3a–i** in $CDCl_3$

	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	NR	X
3a	27.70	197.72	128.93	162.01	15.91	148.10	119.04	129.23	135.83	30.17	20.69
3b	27.94	197.65	131.93	165.36	16.69	154.34	118.60	124.91	144.44	31.92	
3c	28.14	198.18	128.56	161.20	16.06	145.39	114.05	120.98	158.56	29.81	55.31
3d	27.92	198.01	129.61	162.80	16.34	149.54	120.88	131.85	119.25	30.60	
3e	27.56	198.17	130.21	162.33	17.13	146.03	118.03	129.53	135.47	[a]	20.83
3f	27.45	198.29	130.94	163.15	17.38	147.55	117.77	128.97	125.40	[b]	
3g	27.61	198.07	130.49	162.54	17.21	147.55	119.74	131.89	118.64	[c]	
3h	27.91	198.13	128.96	160.57	16.69	143.84	114.04	120.17	158.24	[d]	55.20
3i	28.15	198.30	128.46	160.80	16.32	145.32	114.03	129.56	158.10	[e]	55.31

[a] NBn group: 49.82 (CH_2), 137.21 (*ipso*), 127.54 (*ortho* or *para*), 128.71 (*meta*), 127.32 (*para* or *ortho*). [b] NBn group: 50.45 (CH_2), 137.40 (*ipso*), 127.38 (*para*), 127.57 (*meta*), 128.76 (*ortho*). [c] NBn group: 49.71 (CH_2), 127.34, 127.75, 128.80. [d] NBn group: 48.46 (CH_2), 136.46 (*ipso*), 127.22, 127.65, 128.71. [e] 2,4-diMeOBn group: 42.66, 55.28, 55.34, 98.57, 103.97, 116.88, 120.80, 160.80.

carbon chemical shifts of the methyl group in CH_3CO with the analogous chemical shift of the methyl group in pentane-2,3,4-trione 3-phenylhydrazone allows a presumption that the major form has the arrangement N–H···N (for description of the method see ref. 4). The ^1H, ^{13}C and ^{15}N NMR parameters of products **3a–i** are given in Tables 1–3.

The ^{15}N NMR investigation of compounds **3e** and **3f** in deuteriochloroform solution showed that these substances exist as approximately equimolar mixtures of azo and hydrazone tautomers. Fig. 1 shows the ^1H–^{15}N HMBC spectrum of compound **3f-^{15}N** with visible interactions between NH proton and all the three nitrogen atoms, inclusive of equivalent coupling constants $J(^{15}N,^1H)$, giving thus a further piece of evidence of equivalent proportion of azo and hydrazone tautomers. The equivalence of coupling constants $J(^{15}N1,^1H)$ and $J(^{15}N3,^1H)$ was confirmed in the case of compound **3f-^{15}N** also by means of ^{15}N INEPT and ^{15}N spectra measured without proton decoupling (one-dimensional experiments realised with digital resolution better than 0.6 Hz point^{-1}).

The change in magnitude of individual coupling constants, and thereby their usefulness for estimates of the position of the azo–hydrazone tautomeric equilibrium, was demonstrated in the case of products **3g** and **3h**. The methoxy derivative **3h** exhibits a shift of tautomeric equilibrium towards the azo form

Table 3 ^{15}N NMR parameters of the compounds **3a–I** and **4a–f** in $CDCl_3$

	$\delta(^{15}N1)$	$\delta(^{15}N2)$	$\delta(^{15}N3)$	X	$^1J(^{15}N, ^1H)$/Hz
3a (major)	−35.4	72.7	−216.7		62.4 $^1J(^{15}N3,^1H)$
3a (minor)			−264.6		
3b	−82.6	57.8	−185.7	−11.5	
3c (major)	−16.5	82.5	−236.6		75.1 $^1J(^{15}N3,^1H)$
3c (minor)			−265.1		
3d	−41.2	74.0	−216.3		
3e	−80.0	50.6	−172.7		
3f	−97.6[a]	42.5[b]	−158.5		42.5 $^1J(^{15}N1,^1H)$ 41.7 $^1J(^{15}N3,^1H)$
3g	−79.4	53.1	−175.5		32.5 $^1J(^{15}N1,^1H)$ 53.2 $^1J(^{15}N3,^1H)$
3h	−42.1	68.4	−203.9		18.9 $^1J(^{15}N1,^1H)$ 67.4 $^1J(^{15}N3,^1H)$
3i	80.5	104.4	−220.1		
4a	−43.5	72.8	−211.9		57.4 $^1J(^{15}N3,^1H)$
4b[c]	−102.4	46.5	−159.9	−12.3	
4c	−18.4	82.8	−232.2		72.3 $^1J(^{15}N3,^1H)$
4d	−64.5	Not detected	−180.7		
4e	−45.5	71.7	−183.1		
4f	−13.2	88.6	−201.9		

[a] $^1J(^{15}N1,^{15}N2)$ = 12.7 Hz. [b] $^2J(^{15}N2,^1H)$ = 4 Hz. [c] $^2J(^{15}NO_2,^1H)$ = 3.5 Hz.

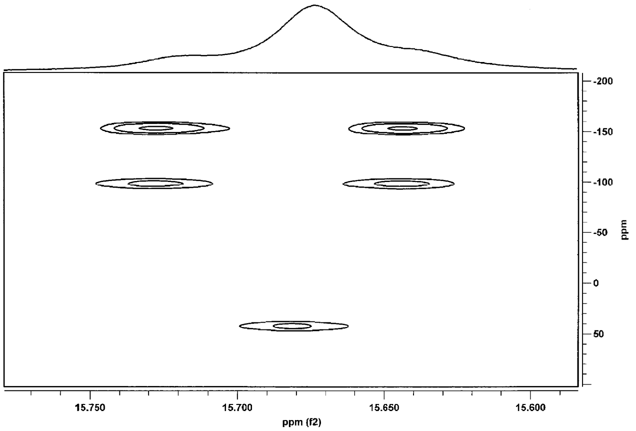
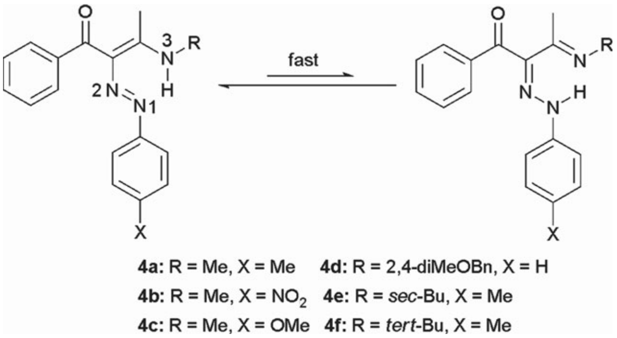


Fig. 1 ^{1}H–^{15}N HMBC spectrum of **3f-^{15}N** in $CDCl_3$.

[in accordance with this, the values of $\delta(^{15}N1)$ are shifted downfield and $\delta(^{15}N3)$ upfield, respectively; the values of coupling constants cease to be equivalent: the value of $J(^{15}N3,^{1}H)$ increased and that of $J(^{15}N1, ^{1}H)$ decreased]. Bromo derivative **3g** shows an opposite trend: the chemical shift $\delta(^{15}N1)$ is shifted upfield and $\delta(^{15}N3)$ downfield, respectively, as compared with the methoxy derivative; the value of $J(^{15}N3,^{1}H)$ decreased and that of $J(^{15}N1,^{1}H)$ increased. Table 3 shows that the position of tautomeric equilibrium of substance **3g** is comparable with that of methyl derivative **3e**.

From the point of view of the substitution effect of the amino group upon the tautomeric equilibrium we can see an increase in content of hydrazone form in the order of N–CH_3 < N–CH_2Ph < N–Ph. However, if the phenyl group of the benzyl grouping is substituted at 2- and 4-positions with methoxy groups, then the product of reaction of enaminone **1c** with 4-methoxybenzenediazonium tetrafluoroborate exists as practically pure azo compound **3i** in $CDCl_3$ solution.



Scheme 4

Also compounds **3e–h** exist in $CDCl_3$ solution as mixtures of two forms. However, due to a very low proportion of the minor form in the tautomeric mixture and to the overlap of its signals with signals of major form, it was only possible to obtain the chemical shift of NH proton, which does not allow any conclusions to be made about its structure.

Similar conclusions concerning the position of azo–hydrazone tautomeric equilibrium as those in the case of acetylacetone derivatives can also be drawn in the case of azo coupling products of 3-methylamino-1-phenylbut-2-en-1-one (Scheme 4). The difference is that products **4a–f** exist in $CDCl_3$ solution in the form of only one isomer. With regard to the nonchanging value of $\delta(^{13}C{=}O)$ it can be stated that the carbonyl group is not affected by the tautomerism (see Table 5), wherefrom it can be inferred that the isomer possesses intramolecular hydrogen bond of N$\cdots$H–N type. The ^{15}N, ^{1}H and ^{13}C NMR parameters of products **4a–f** are presented in Tables 3–5.

Comparison of ^{15}N NMR parameters of products **4a**, **4e** and **4f** (Table 3) shows that branching of the chain of the substituent at the amino group does not significantly affect the position of tautomeric equilibrium; the *tert*-butyl group favours the azo compound slightly more than *sec*-butyl group does.

Comparison of products **3a–c** with their analogues **4a–c** shows that replacement of methyl group at 1-position of the enaminone grouping by phenyl group has virtually no effect on the position of tautomeric equilibrium.

Structure of azo coupling products in the solid phase

An ORTEP[10] view of compound **3a** is given in Fig. 2, while the structures of the other compounds **3c,f** and **4a–c,e,f** are given in the ESI.‡ All the structures of both series **3a–c,f** and **4a–c,e,f** derived from acetylacetone and benzoylacetone, respectively, consist of a mixture of two tautomeric forms. Because both the amino–diazenyl and imino–hydrazone heterodienic fragments are tautomeric systems which display an extended π-delocalization, it is almost impossible to determine the tautomeric ratios only from the analysis of the bond distances within the chelate rings. Accordingly, these ratios have been calculated from the refined occupancies of both tautomeric hydrogens. Although the proton positions can only be localized with an accuracy some ten times smaller than those of other heavy atoms (C, N and O), using data collected at low temperature, it was possible to refine both the hydrogens, with partial

Table 4 ^{1}H NMR spectra of the compounds **4a–f** in $CDCl_3$

	H-4	H-6	H-7	H-8	H-10	H-11	H-12	R	X	NH
4a	2.49 s	7.75–7.77 m	7.35–7.37 m	7.41–7.44 m	7.16–7.18 m	7.05–7.06 m		3.15 s	2.27 s	14.93 br s
4b	2.43 s	7.81–7.83 m	7.41–7.44 m	7.50–7.54 m	7.23–7.27 m	8.10–8.13		3.32 s		15.40 br s
4c	2.54 s	7.72–7.73 m	7.34–7.37 m	7.40–7.43 m	7.23–7.26 m	6.78–6.81 m		3.13 s	3.75 s	14.59 br s
4d	2.58 s	7.78–7.80 m	7.35–7.39 m	7.42–7.46 m	7.12–7.14 m	7.18–7.24 m	7.03–7.07 m	[a]		15.41 br s
4e	2.54 s	7.75–7.77 m	7.31–7.38 m	7.40–7.44 m	7.14–7.17 m	7.05–7.07 m		[b]	2.27 s	15.29 br s
4f	2.67 s	7.71–7.72 m	7.31–7.34 m	7.36–7.39 m	7.18–7.19 m	7.03–7.05 m		1.50 s	2.26 s	15.28 br s

[a] 4.60 (s, 2H), 6.47–6.51 (m, 2H), 7.18–7.24 (m). [b] *sec*-Butyl: 0.98 (t, 3H, J = 7.4 Hz), 1.28 (d, 3H, J = 6.4 Hz), 1.66 (qv, 2H, J = 7.0 Hz), 3.78 (m, 1H, J = 6.0 Hz).

Table 5 ^{13}C chemical shifts of the compounds **4a–f** 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	R	X
4a	193.56	129.36	163.74	16.26	141.07	130.04	127.07	130.24	147.67	119.08	129.44	135.77	31.39	20.86
4b	192.94	132.93	166.16	16.85	139.28	130.12	127.52	131.47	143.92	117.72	125.08	153.03	33.50	
4c	193.77	128.48	162.51	16.07	141.56	130.00	129.93	127.01	145.08	121.06	114.01	158.39	30.36	55.27
4d	193.40	129.76	162.50	16.53	140.80	130.24	129.95	125.46	149.23	118.65	128.70	127.00	[a]	20.86
4e	193.66	128.82	160.92	16.28	141.27	130.06	129.45	127.00	147.94	119.02	129.45	135.75	[b]	20.86
4f	193.81	128.31	160.68	18.56	141.85	129.72	129.64	126.80	149.30	119.71	129.28	136.18	[c]	20.81

[a] 2,4-diMeOBn group: 44.42, 55.14, 55.24, 98.48, 103.95, 117.30, 129.61, 158.06, 160.65. [b] *sec*-Butyl group: 10.12, 20.75, 30.07, 51.90. [c] *tert*-Butyl group: 30.14, 54.20.

occupancies, situated in a double well potential, obtaining, for all compounds, similar tautomeric ratios ranging from 82/18 to 91/9%. The different values obtained from data in solution can be certainly ascribed to the interactions of molecules of solvent with the atoms involved in the hydrogen bonds.

All compounds are N1-aryl and N3-alkyl derivatives and display intramolecular N1–H···N3/N3–H···N1 short hydrogen bonds assisted by resonance (RAHB),[11] extended conjugations within the enamino C1=C2–N3 moiety and weaker delocalisations within the diazenyl N1=N2–C1 group, as shown by the bond orders given in Tables 6 and 7.

In all structures, the hydrogen bonded N1=N2–C1=C2–N3H/HN1–N2=C1–C2=N3 heterodienic systems exhibit quite homogeneous structural features irrespective of the chemical differences within the series **3a–c,f** and **4a–c,e,f** because the distances are bound to be weighed average values of both the delocalized tautomeric fragments. Accordingly, it is almost impossible to define the effects of the *para*-substituents (H, CH_3, OCH_3 and NO_2) on the N1-phenyl ring and on the N1···N3 hydrogen bond distances which are confined in the narrow range of 2.56–2.60 Å. Conversely, in the previous structures of $N3–H_2$ amino derivatives,[6,12–14] the *p*-substituents at the N1-phenyl ring are able to influence the π-delocalizations which are related to a wider range of N1···N3 distances of 2.56–2.64 Å. In these compounds it has been shown, in fact, that the electron withdrawing substituents favour the equalization of N1 and N3 proton affinities and then the shortening of N1···N3 hydrogen-bond distances. Furthermore, also in the two reported structures having aryl substituent both at N1 and N3,[8,14] the substituents on the phenyl rings are able to cause dramatic structural changes. For instance, in both compounds[8,14] the tautomeric equilibrium is shifted toward the imino–hydrazone form, but the N1···N3 distances display the rather different values of 2.479(3) and 2.611(2) Å. These data could be consistent with the different electronic properties of the substituents on the N1- and N3-phenyl rings, because the first compound is a N1-phenyl, N3-*p*-MeO-phenyl[8] derivative while the latter contains the N1-*p*-Br-phenyl and N3-phenyl groups.[14] These results suggest that in amino–diazenyl and imino–hydrazone heterodienic systems the tautomeric equilibrium and the intramolecular N1···N3 hydrogen bond shortening can be determined by the different proton affinities of the nitrogens involved in the intramolecular N–H···N hydrogen bonds. Conversely, in the present N3-alkyl derivatives, the delocalisations within the heterodienic systems and the superimposition of two tautomeric forms do not clarify the effects of the *para*-substituents at the N1-phenyl ring on the N1···N3 hydrogen bond distances.

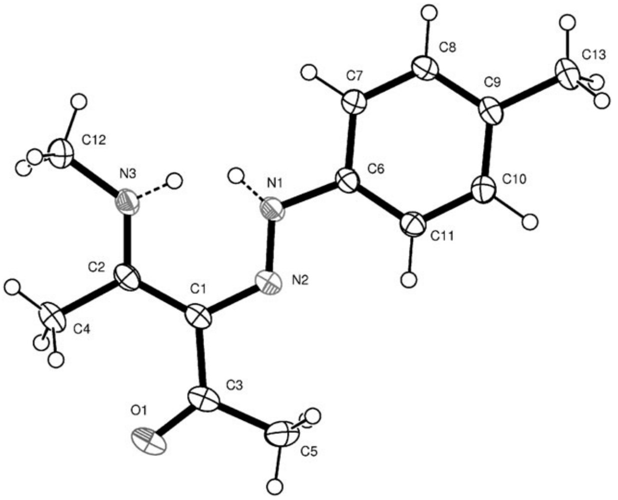


Fig. 2 ORTEP view of compound **3a**. Thermal ellipsoids are drawn at 40% probability level. Both tautomeric hydrogens linked to N1 and N3 atoms, are displayed.

Table 6 Selected bond distances (Å)/bond orders (*in italic*), bond angles and torsion angles (°) and hydrogen bond parameters for structures of acetylacetone derivatives (**3a–c,f**)

Distances	3a	3b	3c	3f
N1–N2	1.284(1)/*1.63*	1.294(1)/*1.56*	1.289(2)/*1.60*	1.284(1)/*1.63*
N2–C1	1.377(2)/*1.18*	1.361(2)/*1.28*	1.372(2)/*1.21*	1.377(1)/*1.18*
C1–C2	1.432(1)/*1.29*	1.437(1)/*1.26*	1.429(2)/*1.30*	1.431(1)/*1.29*
N3–C2	1.316(1)/*1.59*	1.318(2)/*1.58*	1.317(2)/*1.58*	1.315(1)/*1.60*
N1–C6	1.421(2)	1.413(2)	1.421(2)	1.424(1)
C1–C3	1.465(2)	1.472(2)	1.468(2)	1.462(2)
C3–O1	1.227(2)	1.230(2)	1.223(2)	1.232(1)

Hydrogen bonds				
N3H/N1H (ratio)	87/13	86/14	87/13	83/17
N1···N3	2.565(1)	2.585(1)	2.576(2)	2.565(1)
N1–H	0.90(9)	0.72(11)	0.92(12)	1.00(8)
N3–H	0.91(2)	0.88(2)	0.89(2)	0.94(2)
N1–H···N3	120(8)	120(11)	121(11)	118(6)
N3–H···N1	139(2)	135(2)	137(2)	141(2)

Table 7 Selected bond distances (Å)/bond orders (*in italic*), bond angles and torsion angles (°) and hydrogen bond parameters for structures of benzoylacetone derivatives (**4a,b,c–f**)

Distances	**4a**	**4b**	**4c**	**4e**	**4f**
N1–N2	1.289(1)/*1.60*	1.297(2)/*1.54*	1.284(1)/*1.63*	1.283(2)/*1.64*	1.286(2)/*1.62*
N2–C1	1.377(2)/*1.18*	1.359(2)/*1.29*	1.379(2)/*1.17*	1.373(2)/*1.20*	1.375(2)/*1.19*
C1–C2	1.419(2)/*1.36*	1.445(2)/*1.22*	1.422(2)/*1.34*	1.429(2)/*1.30*	1.431(2)/*1.29*
N3–C2	1.322(2)/*1.55*	1.312(2)/*1.62*	1.322(2)/*1.55*	1.317(2)/*1.58*	1.316(2)/*1.59*
N1–C11	1.422(2)	1.413(2)	1.424(2)	1.418(2)	1.420(2)
C1–C3	1.480(2)	1.470(2)	1.470(2)	1.463(2)	1.468(2)
C3–O1	1.231(2)	1.230(2)	1.232(2)	1.229(2)	1.225(2)

Hydrogen bonds					
N3H/N1H (ratio)	82/18	83/17	85/15	91/9	83/17
N1···N3	2.578(1)	2.575(2)	2.601(2)	2.562(2)	2.579(2)
N1–H	0.94(9)	0.93(10)	0.86(10)	0.98(23)	0.93(8)
N3–H	0.93(2)	0.90(2)	0.92(2)	0.94(2)	0.92(3)
N1–H···N3	122(7)	126(8)	130(9)	128(19)	119(6)
N3–H···N1	139(2)	138(2)	137(2)	138(2)	139(2)

Conclusions

The reaction products of 4-methylaminopent-3-en-2-one and benzenediazonium ions substituted at 4-position exist in deuteriochloroform solution as mixtures of *E*/*Z* isomers with the predominating *Z* isomer having an intramolecular hydrogen bond of N–H···N type. The major isomer is a mixture of azo and hydrazone tautomers (38–55% hydrazone form). The amount of azo form depends on the substituent in the diazonium salt and decreases in the order of OMe > Me > Br > NO_2. Isomer *E* is practically pure tautomer azo–enamino.

The transition from 4-methylaminopent-3-en-2-one to 3-methylamino-1-phenylbut-2-en-1-one does not cause any significant changes in position of the tautomeric equilibrium, except for the fact that the products derived from benzoylacetone form only one isomer, *Z*, in deuteriochloroform solution, this isomer being a tautomeric mixture (32–63% hydrazone form).

The position of the azo–hydrazone tautomeric equilibrium in the case of *N*-substituted β-enaminones in $CDCl_3$ solution is most strongly affected by substitution at the nitrogen atom of the starting enaminone. The content of azo form decreases in the order of N–CH_3 > N–CH_2Ph > N–Ph. Substituents at the phenyl group of benzyl grouping also affect the tautomeric equilibrium: the 2,4-dimethoxybenzyl derivative exists in $CDCl_3$ solution as practically pure azo compound. Branching in substituents at nitrogen (Me, *sec*-Bu, *tert*-Bu) has no significant effect upon the position of tautomeric equilibrium; only the *tert*-Bu slightly favours the azo form.

In the solid phase, both **3** and **4** products exist predominantly as azo compounds (82–91%) and exclusively as *Z* isomers. Neither substitution of diazonium salt nor that at N3 nitrogen atom seem to affect significantly the position of tautomeric equilibrium. On the other hand, in all the structures the weighed superimposition of both the hydrogen bonded N1=N2–C1=C2–N3H/ HN1–N2=C1–C2=N3 heterodienic fragments do not allow to well define the effects of the substituents at the N1-phenyl ring both on the N1···N3 hydrogen bond distances and on the bond lengths in the heterodienic systems within the series **3a–c,f** and **4a–c,e,f**.

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 spectroscopy

The NMR spectra were measured using Bruker AMX 360 (360.14 MHz for ^{1}H, 90.57 MHz for ^{13}C and 36.50 MHz for ^{15}N) and Bruker Avance 500 (500.13 MHz for ^{1}H, 125.77 MHz for ^{13}C and 50.69 MHz for ^{15}N) at laboratory temperature. Hexamethyldisiloxane was used as the internal standard for ^{1}H (δ 0.05 in $CDCl_3$).

The ^{13}C NMR spectra were standardised by means of the central signal of the deuteriochloroform triplet (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 *gs* 2D ^{1}H–^{15}N HMBC processed in the magnitude mode. The gradient ratios were 70 : 30 : 50.1. Experiments were performed with the 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 $J(^{15}N,^{1}H)$ 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 ^{1}H–^{15}N HMBC spectra.

The carbon NMR spectra were measured in a standard way and by means of the APT pulse sequence (spectral width 26.455 kHz, acquisition time 1.238 s, zero filling to 64 k and line broadening 1 Hz prior 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, 2 k × 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, 2 k × 160 zero filled to 2 k × 1 k, sinebell squared in both dimensions) each processed in the magnitude mode.

X-Ray structure determinations

The crystal data for compounds **3a–d,3f**, **4a–c,4e,f** were collected using a Nonius Kappa CCD diffractometer with graphite-monochromated Mo-Kα radiation and corrected for Lorentz and polarization effects. The structures were solved by direct methods (SIR97[15]) and refined using full-matrix least squares. All non-hydrogen atoms were refined anisotropically and hydrogens isotropically except the methylic hydrogen atoms of compound **4f** which were included on calculated positions riding on their carrier atoms. In all compounds the difference Fourier map 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 related nitrogen atoms was successfully attempted giving the final occupancy factors in the range 82–91% for H3 and 18–9% for H1.

All the calculations were performed using SHELXL-97[16] and PARST[17] implemented in WINGX[18] system of programs. The crystal data and refinement parameters are summarized in

Table 8 Crystal data

Compound	**3a**	**3b**	**3c**	**3f**
Formula	$C_{13}H_{17}N_3O$	$C_{12}H_{14}N_4O_3$	$C_{13}H_{17}N_3O_2$	$C_{18}H_{19}N_3O$
M	231.30	262.27	247.30	293.36
System	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P\bar{1}$
a/Å	6.6026(1)	10.2904(2)	6.9786(2)	8.1028(2)
b/Å	12.9320(2)	8.7167(2)	14.2655(5)	10.4312(2)
c/Å	15.1197(3)	14.0155(3)	13.2947(6)	10.4731(2)
α/°	90	90	90	67.932(1)
β/°	102.1089(9)	100.9315(9)	101.364(1)	76.578(1)
γ/°	90	90	90	71.720(1)
U/Å^3	1262.27(4)	1234.35(5)	1297.58(8)	772.36(3)
Z	4	4	4	2
D_c/g cm^{-3}	1.217	1.411	1.266	1.261
T/K	150	150	150	150
μ/cm^{-1}	0.80	1.05	0.88	0.80
θ_{min}–θ_{max}/°	3.50–28.00	2.00–28.00	3.30–28.00	2.67–30.00
Unique reflns	3027	2976	3058	4472
R_{int}	0.033	0.031	0.029	0.029
Observed reflns [$I > 2\sigma(I)$]	2594	2556	2368	3588
R (obs. reflns)	0.0421	0.0396	0.0454	0.0432
wR (all reflns)	0.1211	0.1169	0.1256	0.1242
S	1.070	1.078	1.028	1.052
$\Delta\rho_{max}$; $\Delta\rho_{min}$/ e Å^{-3}	0.22; –0.22	0.24; –0.25	0.29; –0.27	0.24; –0.20

Compound	**4a**	**4b**	**4c**	**4e**	**4f**
Formula	$C_{18}H_{19}N_3O$	$C_{17}H_{16}N_4O_3$	$C_{18}H_{19}N_3O_2$	$C_{21}H_{25}N_3O$	$C_{21}H_{25}N_3O$
M	293.36	324.34	309.36	335.44	335.44
System	Orthorhombic	Monoclinic	Orthorhombic	Monoclinic	Orthorhombic
Space group	$P2_12_12_1$	$P2_1/c$	$Pbca$	$P2_1/n$	$P2_12_12_1$
a/Å	7.7167(1)	8.0955(1)	13.6403(2)	8.6915(2)	8.5205(2)
b/Å	10.8923(1)	9.5542(2)	9.6489(2)	17.1912(4)	12.6244(3)
c/Å	18.8973(3)	20.4491(4)	24.3685(5)	13.2188(3)	18.1441(4)
α/°	90	90	90	90	90
β/°	90	98.2804(5)	90	101.066(1)	90
γ/°	90	90	90	90	90
U/Å^3	1588.22(4)	1565.94(5)	3207.2(1)	1938.39(8)	1951.69(8)
Z	4	4	8	4	4
D_c/g cm^{-3}	1.227	1.376	1.281	1.149	1.142
T/K	150	150	150	295	295
μ/cm^{-1}	0.78	0.97	0.85	0.72	0.71
θ_{min}–θ_{max}/°	2.80–30.00	2.50–30.00	2.70–28.00	4.40–27.00	3.93–27.00
Unique reflns	4544	4463	3847	4180	4208
R_{int}	0.051	0.058	0.033	0.034	0.036
Observed reflns [$I > 2\sigma(I)$]	4176	3343	3084	3266	3301
R (obs. reflns)	0.0368	0.0493	0.0391	0.0519	0.0440
wR (all reflns)	0.0932	0.1316	0.1026	0.1487	0.1213
S	1.022	1.037	1.038	1.014	1.019
$\Delta\rho_{max}$; $\Delta\rho_{min}$/e Å^{-3}	0.17; −0.12	0.24; −0.22	0.22; −0.18	0.34; −0.16	0.15; −0.16

Table 8. Selected bond distances/*bond orders*, bond angles and hydrogen bond parameters are given in Tables 6 and 7. Pauling's bond order[19] or, more exactly, bond number, *n*, is evaluated by the formula $d(n) = d(1) - c \log n$, where $d(n)$ and $d(1)$ are the bond lengths for $n = n$ and 1, respectively, and *c* is a constant to be evaluated for each type of chemical bond. The pure single and double bond distances have been retrieved from ref. 20.

CCDC reference numbers 633157–633165.

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b613346k

Materials

Dichloromethane and diisopropyl ether were purchased dry from Fluka and used without change. Anhydrous sodium acetate was purchased commercially and was used without change.

The diazonium tetrafluoroborates were prepared by a known procedure.[5]

Aniline (95% ^{15}N) and sodium nitrite (95% ^{15}N) were purchased from Aldrich.

^{15}N 4-Nitroaniline was prepared in the standard way[21] from ^{15}N aniline.

4-Methylaminopent-3-en-2-one (1a). This was prepared according to the procedure described in ref. 22; bp 54–55 °C/0.60 kPa, lit.[22] 99–100 °C/2.53 kPa.

^{1}H NMR (CDCl$_3$, 360.14 MHz): δ 1.11 (s, 3H, CH$_3$), 1.14 (s, 3H, CH$_3$CO), 2.11 (d. 3H, J = 5.3 Hz, NHCH$_3$), 4.17 (s, 1H, =CH), 9.92 (br s, NH).

4-Benzylaminopent-3-en-2-one (1b). The substance was prepared from acetylacetone and benzylamine in toluene with sulfuric acid as the catalyst. The water formed in the reaction was azeotropically distilled off. After 7 h, the solvent was distilled off. According to NMR, the obtained red oil was sufficiently pure for subsequent reactions. Yield 79%.

^{1}H NMR (CDCl$_3$, 360.14 MHz): δ 1.87 (s, 3H, CH$_3$), 2.00 (s, 3H, CH$_3$CO), 4.41 (d, 2H, CH$_2$, J = 6.4 Hz), 5.02 (s, 1H, =CH), 7.20–7.26 (m, 3H, CH$_{Ar}$), 7.28–7.33 (m, 2H, CH$_{Ar}$), 11.15 (br s, 1H, NH). ^{13}C (CDCl$_3$, 90.57 MHz): δ 18.55 (CH$_3$), 28.58 (CH$_3$), 46.36 (CH$_2$), 95.58 (=CH), 126.36, 127.08, 128.47 (3 × CH$_{Ar}$), 137.72 (C$_q$), 162.81 (=C–N), 195.00 (C=O).

4-(2,4-Dimethoxybenzylamino)pent-3-en-2-one (1c). This compound was prepared from acetylacetone and 2,4-dimethoxybenzylamine in the same way as product **1b**. After the reaction, a part of toluene was distilled off, the solution was cooled, and the separated crystalline solid was collected by suction. The product was purified by vacuum distillation (173–176 °C/0.60–0.70 kPa). Yield 66%.

^{1}H NMR (360.14 MHz, CDCl$_3$): δ 1.93 (s, 3H, CH$_3$), 1.98 (s, 3H, CH$_3$), 3.77 (s, 3H, OCH$_3$), 3.81 (s, 3H, OCH$_3$), 4.33 (d, 2H, CH$_2$, J = 6.4 Hz), 4.96 (s, 1H, =CH), 6.40–6.44 (m, 2H, CH$_{Ar}$), 7.06 (d, 1H, CH$_{Ar}$, J = 8.4 Hz), 11.03 (br s, 1H, NH). ^{13}C (90.57 MHz, CDCl$_3$): δ 18.60 (CH$_3$), 28.65 (CH$_3$), 41.74 (CH$_2$), 55.20, 55.23 (2 × OCH$_3$), 95.23, 98.43, 103.83 (3 × CH$_{Ar}$), 118.57 (C$_q$), 128.54 (CH$_{Ar}$), 157.85, 160.30, 162.84 (3 × C$_q$), 194.57 (C=O).

Calc. for C$_{14}$H$_{19}$NO$_3$ (249.30): C, 67.45; H, 7.68; N, 5.62. Found: C, 67.69; H, 7.51; N, 5.64%.

3-Methylamino-1-phenylbut-2-en-1-one (2a). A 250-ml flask was charged with benzoylacetone (62 mmol) and 33% ethanolic solution of methylamine (120 ml). The mixture was refluxed for 4 h, cooled, and the separated product was collected by suction and recrystallised from *n*-hexane; mp 69–71 °C (ref. 23: 71–72 °C).

^{1}H NMR (360.14 MHz, CDCl$_3$): δ 2.03 (s, 3H, CH$_3$), 2.98 (d, 3H, J = 5.3 Hz, NCH$_3$), 5.66 (s, 1H, =CH), 7.34–7.41 (m, 3H), 7.82–7.85 (m, 2H), 11.30 (br s, 1H, NH).

^{13}C (90.57 MHz, CDCl$_3$): δ 19.06, 29.51, 91.82, 126.69, 127.99, 130.20, 140.36, 165.82, 187.43.

3-(2,4-Dimethoxybenzylamino)-1-phenylbut-2-en-1-one (2b). This compound was prepared in the same way as compound **1c**. Crystallisation from cyclohexane. Yield 92%; mp 84–87 °C. Calc. for C$_{19}$H$_{21}$NO$_3$ (311.38): C 73.29, H 6.80, N 4.50. Found: C 73.34, H 7.02, N 4.56%.

^{1}H NMR (500.13 MHz, CDCl$_3$): δ 2.08 (s, 3H, CH$_3$), 3.77 (s, 3H, OCH$_3$), 3.83 (s, 3H, OCH$_3$), 4.43 (d, 2H, J = 6.3 Hz, CH$_2$), 5.66 (s, 1H, =CH), 6.42–6.45 (m, 2H), 7.12 (d, 1H, J = 8.1 Hz), 7.34–7.40 (m, 3H), 7.83–7.85 (m, 2H), 11.57 (br s, 1H, NH).

^{13}C (125.77 MHz, CDCl$_3$): δ 19.24, 41.96, 55.27, 92.10, 98.52, 103.96, 118.27, 126.74, 127.96, 128.82, 130.16, 140.45, 157.91, 160.42, 164.66, 187.48.

3-(1-Methylpropylamino)-1-phenylbut-2-en-1-one (2c). A mixture of benzoylacetone (25 mmol) and 1-methylpropylamine (200 mmol) was refluxed for 4.5 h. Then the mixture was cooled and the excess amine was distilled off. The residue was dissolved in dichloromethane, dried with Na$_2$SO$_4$ and the solvent was evaporated. According to NMR, the obtained product was sufficiently pure for subsequent reactions. Yield 92%.

^{1}H NMR (500.13 MHz, CDCl$_3$): δ 0.96 (t, J = 7.5 Hz, 3H), 1.25 (d, J = 6.5 Hz, 3H), 1.57–1.63 (m, 2H), 2.07 (s, 3H), 3.52–3.60 (m, 1H), 5.61 (s, 1H), 7.35–7.39 (m, 3H), 7.84–7.86 (m, 2H), 11.47 (br s, 1H).

^{13}C NMR (125.77 MHz, CDCl$_3$): δ 10.30, 19.22, 21.40, 30.48, 50.52, 91.54, 126.66, 127.93, 130.12, 140.33, 163.84, 187.11.

3-*tert*-Butylamino-1-phenylbut-2-en-1-one (2d). This compound was prepared from benzoylacetone in two steps (Scheme 2).

3-Chloro-1-phenylbut-2-en-1-one:[24] A solution of 50 mmol benzoylacetone in 40 ml chloroform was treated with 126 mmol oxalyl chloride added dropwise within *ca.* 30 min with stirring. Then the mixture was refluxed for 2 h. The solvent and excess oxalyl chloride were distilled off in vacuum. The dark tarry residue was fractionated in vacuum to give product boiling at 110–120 °C/1.20 kPa (ref. 25 gives bp 105 °C at 0.40 kPa). Yield 38%.

3-*tert*-Butylamino-1-phenylbut-2-en-1-one: A solution of 19 mmol 3-chloro-1-phenylbut-2-en-1-one in 40 ml diethyl ether was treated with a solution of 38 mmol *tert*-butylamine in 10 ml diethyl ether added dropwise with stirring. The mixture was stirred at room temperature overnight. The separated portion was collected by suction and washed with ether. The solvent was evaporated and the residue was fractionated in vacuum to give 38.5% yield of liquid boiling at 162–166 °C/0.70 kPa; ref. 26 gives bp 50 °C at 1.33 Pa.

^{1}H NMR (500.13 MHz, $CDCl_3$): δ 1.45 (s, 9H), 2.19 (s, 3H), 5.59 (s, 1H), 7.36–7.38 (m, 3H), 7.83–7.84 (m, 2H), 11.95 (br s, 1H).

^{13}C NMR (125.77 MHz, $CDCl_3$): δ 20.85, 30.64, 52.45, 93.01, 126.63, 127.94, 130.09, 140.41, 164.86, 186.69.

3-Decylamino-1-phenylbut-2-en-1-one (2e). A mixture of benzoylacetone (25 mmol) and *n*-decylamine (25 mmol) was refluxed in toluene (30 ml) for 4 h. The solvent was evaporated in vacuum and the residue was fractionated in vacuum to give 62% yield of a yellow wax; mp 30–33 °C, bp 217–220 °C/0.93 kPa. Calc. for $C_{22}H_{35}NO$ (329.52): C 80.19, H 10.71, N 4.25. Found: C 80.04, H 10.81, N 4.40%.

^{1}H NMR (500.13 MHz, $CDCl_3$): δ 0.87 (m, 3H), 1.26–1.42 (m, 14H), 1.633 (quintet, J = 10 Hz, 2H), 2.04 (s, 3H), 3.29 (m, 2H), 5.64 (s, 1H), 7.37–7.38 (m, 3H), 7.83–7.86 (m, 2H), 11.44 (br s, 1H).

^{13}C NMR (125.77 MHz, $CDCl_3$): δ 13.93, 19.20, 22.49, 26.74, 29.12, 29.13, 29.30, 29.37, 29.90, 31.70, 43.17, 91.66, 126.64, 127.91, 130.10, 140.35, 164.67, 187.27.

General procedure of azo coupling reactions

A 100-ml Erlenmeyer flask was charged with 4.4 mmol of the respective enaminone and 30 ml dry diisopropyl ether (**3a–f,I**), or dichloromethane (**3g–h**, **4a–f**). With stirring, 13.2 mmol sodium acetate was added, followed by 4.4 mmol of the respective substituted benzenediazonium tetrafluoroborate. The mixture was stirred at room temperature for a period of 2 to 24 h, depending on the starting reagents used. Then the solid portion was collected by suction, and the filter cake was washed with little dichloromethane. The filtrate was evaporated in vacuum and the residue further purified by recrystallisation.

4-Methylamino-3-(4-methylphenyldiazenyl)pent-3-en-2-one (3a). Reaction time 24 h. Recrystallisation from cyclohexane. Yield 0.69 g (68%); mp 113–115 °C. Calc. for $C_{13}H_{17}N_3O$ (231.29): C 67.51, H 7.41, N 18.17. Found: C 67.73, H 7.69, N 18.45%.

4-Methylamino-3-(4-nitrophenyldiazenyl)pent-3-en-2-one (3b). Reaction time 24 h. Recrystallisation from *n*-hexane–toluene. Yield 0.43 g (37%); mp 152.5–155 °C. Calc. for $C_{12}H_{14}N_4O_3$ (262.26): C 54.96, H 5.38, N 21.36. Found: C 55.25, H 5.16, N 21.41%.

4-Methylamino-3-(4-nitrophenyl[^{15}N1]diazenyl)pent-3-en-2-one (3b-^{15}N1) and 4-methylamino-3-(4-nitrophenyl[^{15}N2]diazenyl)pent-3-en-2-one (3b-^{15}N2). These substances were prepared in the same way as that used for **3b**. The starting 4-nitrobenzenediazonium tetrafluoroborate was isotopically labelled at the N1 nitrogen atom (95% ^{15}N) (for preparation of product **3b**-$^{15}N_\alpha$) or at the N2 nitrogen (25% ^{15}N) (for preparation of product **3b**-$^{15}N_\beta$). Yields (**3b**-$^{15}N_\alpha$) 0.17 g (68%) and (**3b**-$^{15}N_\beta$) 0.13 g (52%); mp 156.5–158 °C for **3b-^{15}N1** and 153.5–155 °C for **3b-^{15}N2**, respectively.

4-Methylamino-3-(4-methoxyphenyldiazenyl)pent-3-en-2-one (3c). Reaction time 24 h. Recrystallisation from cyclohexane. Yield 38%; mp 90–92 °C. Calc. for $C_{13}H_{17}N_3O_2$ (247.29): C 63.14, H 6.93, N 16.99. Found: C 63.10, H 6.81, N 17.12%.

4-Methylamino-3-(4-bromophenyldiazenyl)pent-3-en-2-one (3d). Reaction time 24 h. Recrystallisation from cyclohexane. Yield 29%; mp 84–85.5 °C. Calc. for $C_{12}H_{14}N_3OBr$ (296.16): C 48.67, H 4.76, N 14.19. Found: C 48.42, H 4.67, N 14.12%.

4-Benzylimino-3-(4-methylphenylhydrazono)pentane-2-one (3e). The compound was prepared by a modification of the general procedure. Reaction time 24 h. The filter cake was washed first with little diisopropyl ether and then with dichloromethane. The two filtrates were collected separately. The dichloromethane filtrate contained practically pure product of azo coupling reaction. The evaporation residue obtained from this filtrate was recrystallised from ethanol. Yield 39%; mp 111–113 °C. Calc. for $C_{19}H_{21}N_3O$ (307.39): C 74.24, H 6.89, N 13.67. Found: C 74.25, H 6.77, N 13.68%.

4-Benzylimino-3-phenylhydrazonopentane-2-one (3f). This was prepared in the same way as that used for **3e**. Yield 45%; mp 108–110 °C. Calc. for $C_{18}H_{19}N_3O$ (293.36): C 73.70, H 6.53, N 14.32. Found: C 73.97, H 6.65, N 14.09%.

4-Benzylimino-3-phenylhydrazonopentane-2-one (3f-^{15}N). This was prepared in the same way as that used for **3e**. Enrichment 20% ^{15}N2 and 95% ^{15}N1. Yield 41%; mp 108–109 °C.

4-Benzylimino-3-(4-bromophenylhydrazono)pentane-2-one (3g). Reaction time 3 h. Recrystallisation from cyclohexane. Yield 52%; mp 112–115 °C.

Calc. for $C_{18}H_{18}BrN_3O$ (372.26): C 58.08, H 4.87, N 11.29. Found: C 58.33, H 4.89, N 11.23%.

4-Benzylimino-3-(4-methoxyphenylhydrazono)pentane-2-one (3h). Reaction time 18 h. Recrystallisation from cyclohexane. Yield 63%; mp 95–99 °C. Calc. for $C_{19}H_{21}N_3O_2$ (323.39): C 70.57, H 6.55, N 12.99. Found: C 70.69, H 6.60, N 13.01%.

4-(2,4-Dimethoxybenzylamino)-3-(4-methoxyphenyldiazenyl)pent-3-en-2-one (3i). Reaction time 24 h. Recrystallisation from cyclohexane. Yield 28%; mp 82–89 °C. Calc. for $C_{21}H_{25}N_3O_4$ (383.44): C 65.78, H 6.57, N 10.96. Found: C 66.00, H 6.61, N 10.95%.

3-Methylamino-2-(4-methylphenyldiazenyl)-1-phenylbut-2-en-1-one (4a). Reaction time 24 h. Recrystallisation from cyclohexane. Yield 39%; mp 109.5–111 °C. Calc. for $C_{18}H_{19}N_3O$ (293.36): C 73.70, H 6.53, N 14.32. Found: C 73.71, H 6.77, N 14.41%.

3-Methylamino-2-(4-nitrophenyldiazenyl)-1-phenylbut-2-en-1-one (4b). Reaction time 2 h. Recrystallisation from cyclohexane–toluene. Yield 38%; mp 155.5–157 °C. Calc. for $C_{17}H_{16}N_4O_3$ (324.33): C 62.95, H 4.97, N 17.27. Found: C 63.22, H 4.74, N 17.06%.

3-Methylamino-2-(4-methoxyphenyldiazenyl)-1-phenylbut-2-en-1-one (4c). Reaction time 24 h. Recrystallisation from cyclohexane. Yield 64%; mp 109–110.5 °C. Calc. for $C_{18}H_{19}N_3O_2$ (309.36): C 69.88, H 6.19, N 13.58. Found: C 69.96, H 6.49, N 13.58%.

3-(2,4-Dimethoxybenzylamino)-2-phenyldiazenyl-1-phenylbut-2-en-1-one (4d). Reaction time 24 h. Recrystallisation from cyclohexane–toluene. Yield 51%; mp 129.5–132 °C. Calc. for $C_{25}H_{25}N_4O_3$ (415.49): C 72.27, H 6.06, N 10.11. Found: C 72.47, H 5.93, N 9.90%.

3-(1-Methylpropylamino)-2-(4-methylphenyldiazenyl)-1-phenylbut-2-en-1-one (4e). Reaction time 24 h. Recrystallisation from ethanol. Yield 68%; mp 112–116 °C. Calc. for $C_{21}H_{25}N_3O$ (335.44): C 75.19, H 7.51, N 12.53. Found: C 75.25, H 7.57, N 12.57%.

3-*tert*-Butylamino-2-(4-methylphenyldiazenyl)-1-phenylbut-2-en-1-one (4f). Reaction time 24 h. Chromatography silica/ethyl acetate. Recrystallisation from ethanol. Yield 80%; mp 145–146 °C. Calc. for $C_{21}H_{25}N_3O$ (335.44): C 75.19, H 7.51, N 12.53. Found: C 75.48, H 7.61, N 12.63%.

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