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An NMR and X-ray study of the structure of the azo coupling product of 4-dimethylaminopent-3-en-2-one and benzenediazonium-tetrafluoroborate

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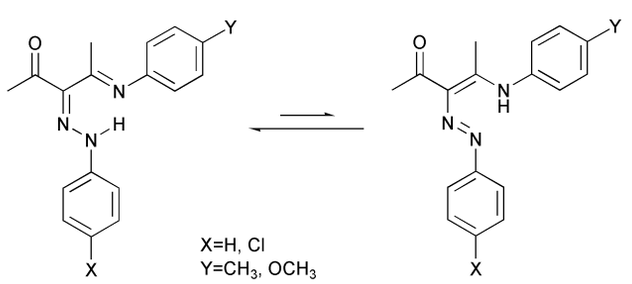
4-Dimethylaminopent-3-en-2-one reacts with two molecules of benzenediazonium-tetrafluoroborate to give compound **1**. The structure of this compound was determined by means of X-ray analysis of its crystal and ^{1}H, ^{13}C and ^{15}N NMR spectra of its solution in $CDCl_3$. The molecule of this compound contains one azo group and one hydrazone group. The substance exists, both in crystal form and in solutions of concentrations above 0.1 mol l^{-1}, in the form of a dimer, in which the pair of molecules are bound by two hydrogen bonds N–H ··· N. On diluting the solution, the dimers decompose, the two forms being in an equilibrium that is rapid on the NMR time scale.

Introduction

In previous papers[1–3] we dealt with studies of the structures of azo coupling products obtained from selected β-enaminones and diazonium ions; these studies were based on ^{1}H, ^{13}C and ^{15}N NMR spectroscopy and X-ray diffraction. The reaction of substituted 4-phenylaminopent-3-en-2-ones with diazonium ions gives the correspondingly substituted 3-phenylhydrazono-4-phenyliminopentan-2-ones,[1] which are in rapid tautomeric equilibrium with the respective azo compounds (Scheme 1).



Scheme 1

The azo coupling products obtained from 4-functionalised benzenediazonium-tetrafluoroborates and 4-aminopent-3-en-2-one or 4-methylaminopent-3-en-2-one exist in $CDCl_3$ solutions in the form of two isomers differing in the isomerism at the "predominantly" C3=C4 double bond and in the arrangement of the intramolecular hydrogen bond, which is N–H ··· N and N–H ··· O in the major and minor isomers, respectively.[1] The major isomer is present at *ca.* 80%, depending on the substituent of the benzenediazonium ion. The major isomer is a mixture of the predominant azo form and less populated hydrazone form, present in a very fast tautomeric equilibrium (Scheme 2).

The content of the azo form is 70–85% and depends only very little on the substituent of the phenylazo group. The equilibrium between the major and minor forms is slow on the NMR time scale, the minor form consisting of a practically pure azo compound. X-Ray diffraction revealed[2] that the 4-chloro and 4-nitro derivatives exist in the crystal in the form of a single geometry isomer, which is an equilibrium mixture of azo and hydrazone forms. Two positions were found for the proton involved in the tautomeric exchange, their populations giving the populations of the tautomers. The content of the hydrazone form estimated in the solid phase is about one half that found in $CDCl_3$ solution (*ca.* 16% and 30% for the *p*-chloro derivative, and 20% and 45% for the 4-nitro derivative, respectively).[1,2]

3-Amino-5,5-dimethylcyclohex-2-en-1-one and its *N*-phenyl derivative react with the *p*-substituted benzenediazonium-tetrafluoroborates in a molar ratio of 1 : 2 even in cases where the starting reactants are present at a ratio of 1 : 1.[3] The azo coupling reaction takes place at the 2 and 4 positions of the starting enaminones. Only in the case of the reaction of 4-methoxybenzenediazonium ion with 3-amino-5,5-dimethylcyclohex-2-en-1-one was the presence of the 1 : 1 product detected in traces.[3] Irrespective of the substituents in both the diazonium ion and enaminone, the group bound at the 2- position is in the hydrazone form. Also the group attached at the 4- position in 3-phenylamino derivatives is present in its tautomeric hydrazone form. The tautomeric forms of the azo coupling products obtained from the 3-amino derivative depend to a certain extent on the substituent in the diazonium ion. While in the cases of 4-methyl- and 4-bromobenzenediazonium reactants the group at the 4- position of the products predominantly exists in hydrazone form, in the case of the 4-methoxy derivative this group is predominantly in the azo form[3] (Scheme 3).

The enaminones studied so far in the context of azo coupling reactions possess a primary or secondary amino group, and the positively charged intermediate formed by attack on the enaminone by the diazonium ion can split off a proton from the nitrogen (Scheme 4).[4]

In the case of an enaminone possessing a tertiary nitrogen atom, such a possibility is not available, and therefore, different behaviour can be expected during the azo coupling reaction. The aim of this work is to investigate such a case.

The reaction of diazonium salt with enaminones containing a tertiary amino group—1-diethylamino-5-arylpenta-1,4-dien-3-ones—was dealt with by Elnagdi and co-workers;[5] however,

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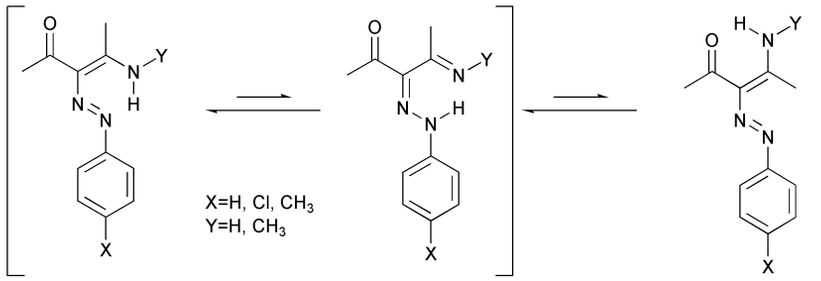
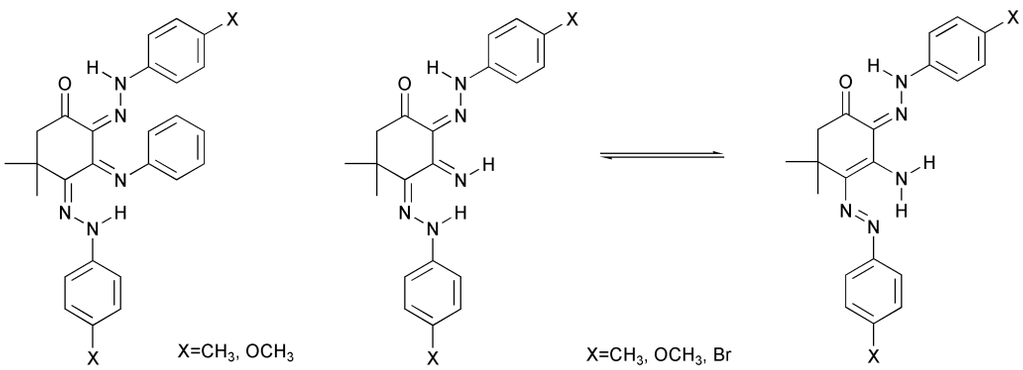
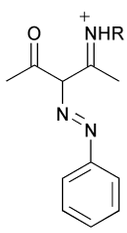


Scheme 2



Scheme 3



Scheme 4

they only isolated the hydrolysis products of primary substances, *viz.* 5-aryl-2-arylhydrazono-3-oxopent-4-enals.

Results and discussion

The reaction of benzenediazonium-tetrafluoroborate with 4-dimethylaminopent-3-en-2-one at a molar ratio of 1 : 1 produces a red substance whose elemental analysis corresponds to the molecular formula $C_{19}H_{21}N_5O$. Solutions of this compound in $CDCl_3$ are not stable, the compound being decomposed within several hours unless the traces of hydrochloric acid present in the solvent used are removed by shaking with solid sodium carbonate.

X-Ray structure determination

An ORTEP[6] view of the prepared compound is shown in Fig. 1. The molecule is built up by two approximately planar moieties, a phenyl β-ketohydrazone and a phenyl diazenyl vinyl dimethylamine, displaying, through their alternate single and double bonds, π-conjugations which can be evaluated in terms of Pauling bond orders.[7] The β-ketohydrazone is about 30% delocalized within the N4(H)–N3=C3 hydrazone fragment, while within the C3–C6=O1 fragment the delocalization is insignificant, in agreement with the structural data of a series of molecules of simple β-ketohydrazones.[8] On the other hand, the diazenyl vinyl dimethylamino moiety displays a more homogeneous π-conjugation of about 33% throughout the fragment. This induces the dimethylamino group to be planar with a consequent rehybridization of N5 nitrogen from sp^3 to sp^2 and a significant shortening of the C2–N5 bond up to 1.343(5) Å.[9]

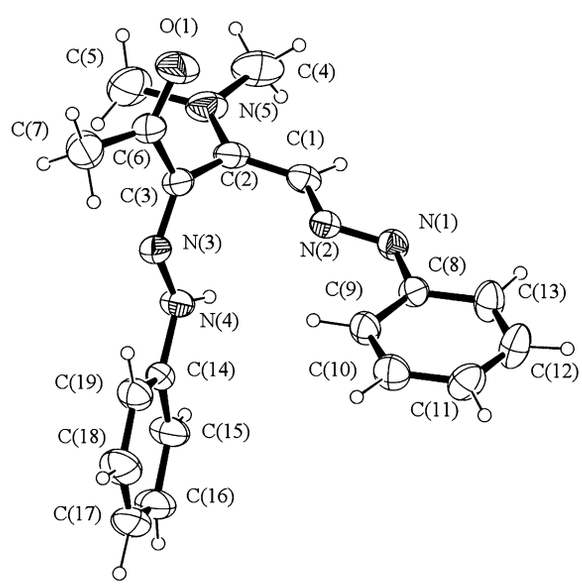


Fig. 1 ORTEP view of compound **1** showing the thermal ellipsoids at 30% probability.

The two planar moieties are mutually rotated around the C2–C3 pure single bond by an angle of −65.4(3)° as determined by the value of the C1–C2–C3–N3 torsion angle. The β-ketohydrazone fragment displays a *zigzag* planar conformation with the N–H in *anti* configuration with respect to the carbonyl C=O group and has the correct geometry for forming, at least in principle, chains of intermolecular N–H ··· O resonance assisted hydrogen bonds (RAHB).[8] This kind of hydrogen bond, however, is not observed in crystal form probably due to the lack of any π-conjugation within the C3–C6=O1 system and for steric reasons. Accordingly, the molecules assume a more favourable packing arrangement where they are linked in dimers by means of N4–H ··· N1 hydrogen bonds with an N4 ··· N1 distance of 3.172(2) Å (Fig. 2). Molecules are coupled around a centre of symmetry. This interaction can be considered a weak N–H ··· N intermolecular hydrogen bond in view of the N ··· N average distance of 2.95 ± 0.10 Å calculated from 284 R,R′–N–H ··· N(sp^2) intermolecular contacts

Table 1 Crystal data

Compound	**1**
Formula	$C_{19}H_{21}N_5O$
M_r	335.41
Crystal system	Monoclinic
Space group	$P2_1/n$
a/Å	10.5524(2)
b/Å	10.8377(2)
c/Å	16.4357(4)
β (°)	101.829(1)
V/Å^3	1839.73(7)
Z	4
D_c/g cm^{-3}	1.211
F(000)	712
μ/cm^{-1}	0.79
Temperature/K	295
Crystal form, colour	prism, red
Crystal size/mm	0.26 × 0.27 × 0.36
θ_{min}–θ_{max}	3.4–28
Measured reflections	8623
Range of h,k,l	−13–13, −14–14, −21–21
Unique reflections	4414
R_{int}	0.021
Obs. reflections [$F^2>2\sigma(F^2)$]	2987
$R(F^2)$ (Obs. reflections)	0.0540
$wR(F^2)$ (All reflections)	0.1634
No. parameters	310
GOF	1.08
$\Delta\rho_{max}$, $\Delta\rho_{min}$	0.15; −0.15

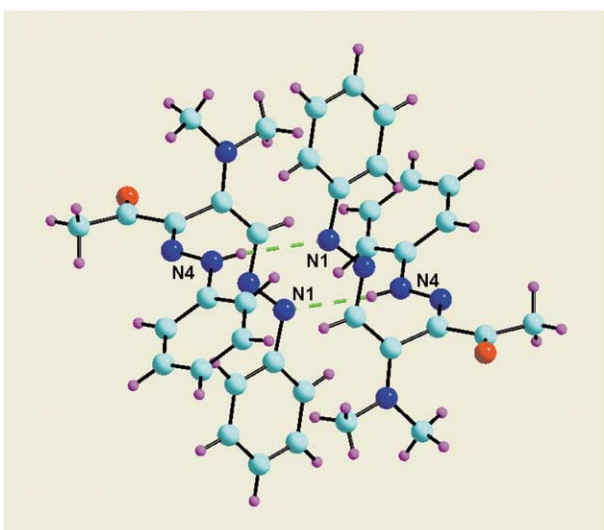


Fig. 2 A couple of molecules of compound **1** linked by intermolecular N4–H ··· N1 hydrogen bonds.

retrieved from the Cambridge Crystallographic Data Base.[10] Crystal data are given in Table 1 †. Selected bond distances and angles are shown in Table 2.

Multinuclear magnetic resonance study in solution

The ^{1}H NMR spectrum ($CDCl_3$, c = 0.2 mol dm^{-3}) of the azo coupling product **1** obtained from benzenediazonium-tetrafluoroborate and 4-dimethylaminopent-3-en-2-one corresponds to the presence of two molecular entities A and B, the former being predominant (*ca.* 98%). The inter-conversion of the two forms A and B is slow on the NMR time scale. The form A contains two different mono-functionalised benzene nuclei and one aliphatic chain. The protons in A were assigned to the individual nuclei with the help of the H,H-COSY spectrum. The spectrum of the molecule also contains a singlet of methine group =CH– with an integral intensity of 1 (δ 6.91). The signal of the dimethylamino group present is very broadened and has a character typical of the given group with hindered rotation (*e.g.* in *N,N*-dimethylamides of acids). The signal of the carbonyl group in the ^{13}C non-decoupled INEPT spectrum is split into a quartet *via* ^2J, which means that a methyl group is present in the vicinity of the carbonyl group. Therefore, the attack by one diazonium ion takes place at the C-3 carbon atom of the starting enaminone while the other diazonium salt attacks the C-5 methyl group in the vicinity of dimethylamino group. From the $\delta(^{15}N)$ values (−228.3 and −32.1; 30.2 and 94.3) it is obvious that the substance A contains one pure hydrazone group and one pure azo group.[11–14] The presence of the hydrazone group is also confirmed by the value of coupling constant $^1J(^{15}N,^1H)$ = 93.6 Hz for the nitrogen atom with $\delta(^{15}N)$ −228.3.

The ^{1}H–^{15}N HMBC spectrum (Fig. 3) clearly shows an interaction between the proton of the =CH– group and both nitrogen atoms of the azo group by means of $^2J(^{15}N, ^1H)$ and $^3J(^{15}N, ^1H)$ ($\delta(^{15}N)$ 30.2 and 94.3 at the concentration of the substance 0.2 mol dm^{-3}); hence the product A has the structure given in formula (**1a**) and not the other possible structure (**1b**), in which the proton of the =CH– group would have to correlate with the nitrogen atoms of hydrazone group.

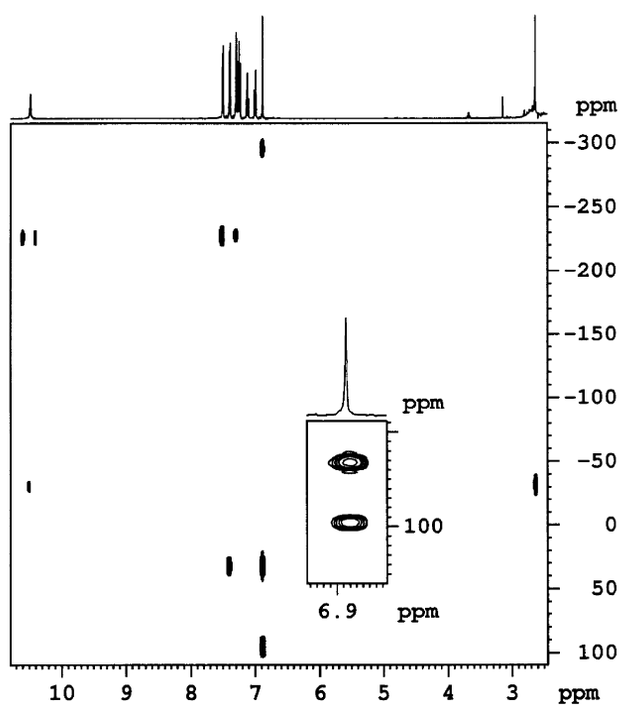


Fig. 3 500 MHz ^{1}H–^{15}N HMBC spectrum of the non labelled compound **1** in $CDCl_3$. Delay for evolution of long range coupling d6 was set to 100 ms.

The acidic proton of the NH group is involved in hydrogen bonding; the chemical shift δ(HN) 10.63 indicates that this is not a firm hydrogen bond of N–H ··· O= type (such as that observed in azo coupling products obtained from ketones and existing in hydrazone form, δ(HN) ~ 15).[1] NMR data of the compound A are presented in Tables 3–5. The other minor form B is an isomer of the major form. This compound could only be characterised by the ^{1}H and ^{15}N chemical shifts (in the isotopically labelled compound).

Concentration and temperature studies

On dilution, the character of the ^{1}H NMR spectrum changes: chemical shifts of some of the protons are changed and the content of component B increases with decreasing concen-

† CCDC reference number 206572. See http://www.rsc.org/suppdata/ob/b3/b303206j/ for crystallographic data in .cif or other electronic format.

Table 2 Selected bond distances (Å), bond angles (°) and torsion angles (°)

N1–N2	1.282(2)	C3–C6	1.484(3)
N1–C8	1.417(2)	C6–O1	1.213(6)
N2–C1	1.359(2)	N3–C3	1.295(2)
C1–C2	1.375(3)	N3–N4	1.326(2)
C2–C3	1.493(3)	N4–C14	1.400(2)
C2–N5	1.343(2)		
C8–N1–N2	113.6(1)	C2–C3–N3	126.5(2)
N1–N2–C1	114.7(1)	C3–N3–N4	121.5(2)
N2–C1–C2	118.3(2)	N3–N4–C14	118.5(1)
C1–C2–C3	120.0(2)		
C9–C8–N1–N2	15.6(2)	C1–C2–C3–N3	−65.4(3)
C8–N1–N2–C1	179.6(1)	C2–C3–N3–N4	−1.8(3)
N1–N2–C1–C2	179.0(2)	C3–N3–N4–C14	170.0(2)
N2–C1–C2–N5	175.9(2)	O1–C6–C3–N3	166.4(2)
N2–C1–C2–C3	−2.6(3)	N3–N4–C14–C19	−13.4(2)
Hydrogen bonding			
N4–H4	N4 ··· N1[i]	H4 ··· N1	N4–H4 ··· N1
0.84(2)	3.172(2)	2.37(2)	161(2)
i: symmetry code:	1 − x, −y, 1 − z		

Table 3 ^{1}H chemical shifts of the compound **1** in $CDCl_3$ (c = 0.2 mol dm^{-3})

$N(CH_3)_2$	H-1	H-5	H-13	H-9	H-8	H-12	H-7	H-11	$N_\alpha H$
2.35–2.66[a]	2.63	6.91	6.99–7.01	7.10–7.13	7.23–7.26	7.27–7.30	7.38–7.40	7.50–7.52	10.63

[a] Near the coalescence point.

Table 4 ^{13}C chemical shifts of the compound **1** in $CDCl_3$ (c = 0.2 mol dm^{-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	C-13	C-14
24.81	195.78	136.53	152.66	124.48	153.91	120.48	128.82	127.01	143.52	114.58	129.36	122.61	39.15

Table 5 ^{15}N NMR parameters of the compound **1** in $CDCl_3$ (c = 0.2 mol dm^{-3})

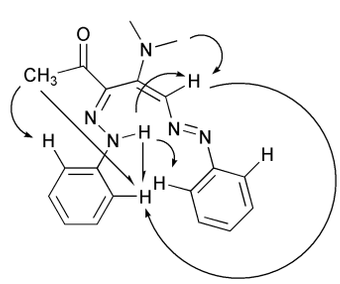
N_α	N_β	N_γ	N_δ	N_ε
−228.3[a]	−32.1[b]	94.3	30.2	−296.1

[a] ^{1}J (^{15}N, ^{15}N) = 10.6 Hz, ^{1}J (^{15}N, ^{1}H) = 93.6 Hz. [b] ^{1}J (^{15}N, ^{15}N) = 10.6 Hz.

tration. The concentration-dependent changes are depicted in Fig. 4a–d. The changes in chemical shifts with changing concentration can be interpreted as follows: the results of X-ray analysis show that the substance in solid state exists in the form of dimers with two intermolecular hydrogen bonds between each pair of molecules. These dimers $(\mathbf{1a})_2$ also exist in solution, being in a kind of equilibrium with the free molecules **1a** (monomer). The chemical exchange between monomers and dimers is rapid on the NMR time scale since the hydrogen bonds binding the molecules in dimers are very weak. However, it is not rapid enough to allow sharp signals to be observed in the spectrum; the signals are somewhat broadened because the monomer and dimer can differ in chemical shifts of corresponding atoms in the ^{1}H, ^{13}C as well as ^{15}N NMR spectra due to different populations of tautomers and different chemical environments. Decreasing concentration shifts the equilibrium in favour of the monomer and *vice versa*. The chemical shifts of protons change continuously in the concentration interval studied (0.1–0.008 mol dm^{-3}). The existence of a monomer–dimer equilibrium was also used to interpret spectral behaviour of 6,11-dimethyl-6*H*-indolo[2,3-*b*]quinoline derivatives.[15]

The effect of cooling the solution was opposite to that of diluting it. A solution of 0.1 mol dm^{-3} **1** was diluted to 0.02 mol dm^{-3} and then cooled in the spectrometer cell. The spectrum of diluted solution after cooling to 273 K agrees quite well with that of the starting solution before dilution (Fig. 5 a–c). Further cooling causes only small changes in chemical shifts of the protons (*cf.* Fig. 5 c,d). On cooling the solution the δ(NH) value changes down-field, which can be explained by strengthening of the intermolecular hydrogen bond N–H ··· N. In accordance therewith, a temperature increase causes a decrease in δ(NH).

The spatial arrangement of the major component at c = 0.2 mol dm^{-3} was studied by means of 2D NOESY and 1D NOE difference experiments. At this concentration the product probably exists almost entirely in the dimer form $(\mathbf{1a})_2$ since a dilution to 0.1 mol dm^{-3} causes only small changes in chemical shifts of the protons and there is an almost negligible amount of the minor component B. The data obtained from the NOE experiments agree with the dimer structure, which was determined by means of X-ray analysis (Fig. 2). The results obtained by interpretation of NOE experiments are graphically presented in Scheme 5.



Scheme 5

Only few data can be obtained about structure of the minor component B since most of the proton signals are overlapped by those of the dimer. With regard to the fact that the relative intensity of signals of the component B depends on

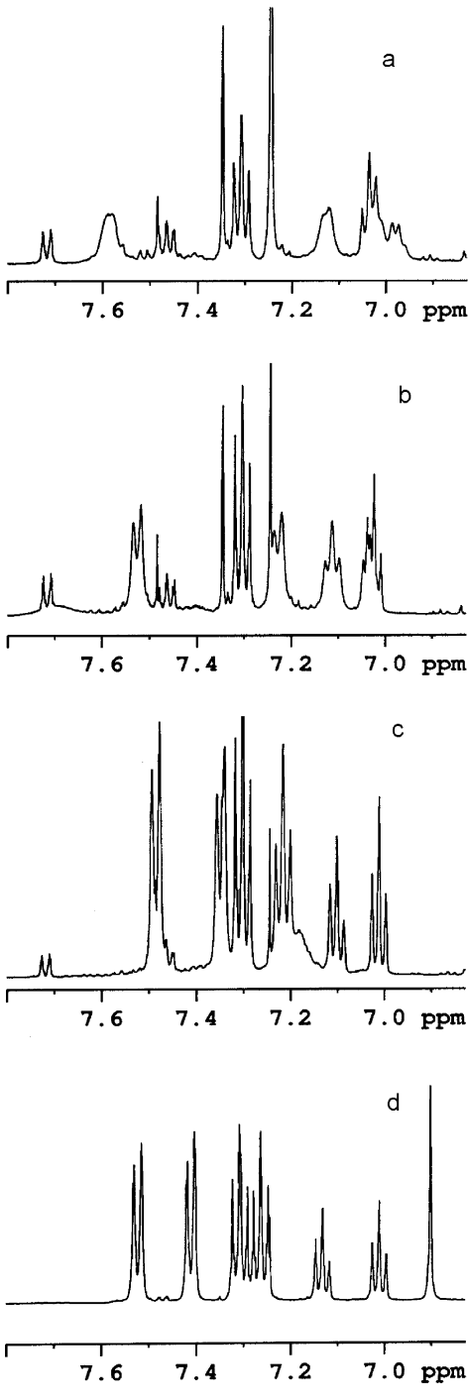


Fig. 4 500 MHz ^{1}H NMR spectrum of the compound **1** in $CDCl_3$ at various concentrations: (a) 8 mmol dm^{-3}; (b) 30 mmol dm^{-3}; (c) 75 mmol dm^{-3}; (d) 200 mmol dm^{-3}.

concentration, this species could be a monomer **1c** with a geometry arrangement different from that of the monomer **1a** formed by dissociation of the dimer. The multiplet with chemical shift δ 7.71–7.73 has a form characteristic of *ortho* protons in a monosubstituted benzene ring. Using the 1D selective TOCSY pulse sequence, we also succeeded in obtaining the chemical shifts of the protons which form a spin system with it, *i.e. meta* and *para* protons: 7.45–7.48 and 7.28–7.32. Another piece of information that could be obtained about this molecule includes the chemical shifts of nitrogen atoms correlating with the proton mentioned: −166.5 and −230. Measurement of ^{13}C chemical shifts of the minor component was unsuccessful due to chemical exchange even after long-time acquisitions. It is impossible to determine the structure of the minor component

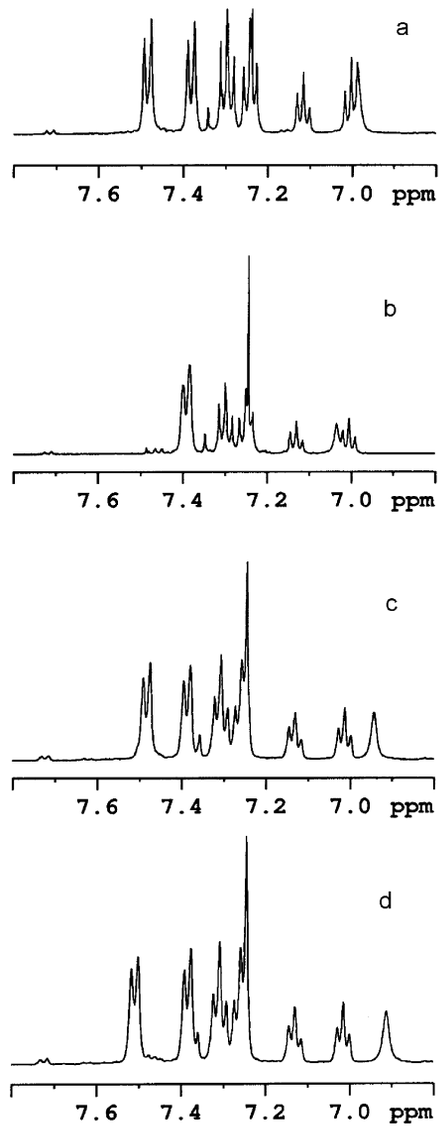
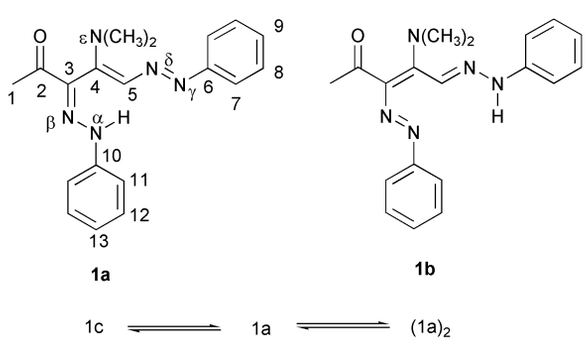


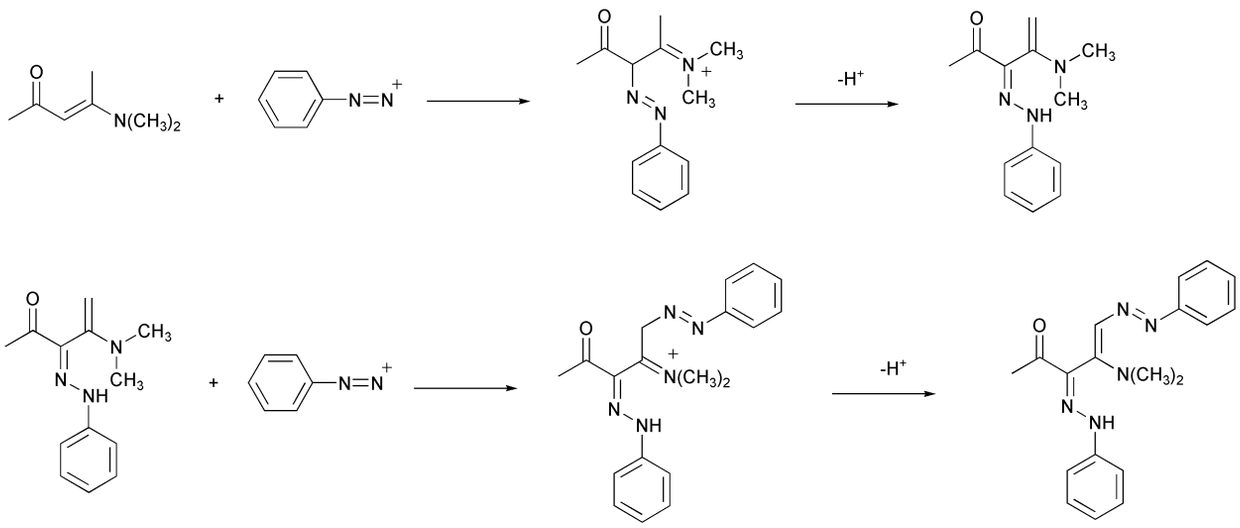
Fig. 5 500 MHz ^{1}H NMR spectrum of the compound **1** in $CDCl_3$ at various temperatures: (a) c = 0.1 mol dm^{-3}, 293 K; (b) c = 0.02 mol dm^{-3}, 293 K; (c) c = 0.02 mol dm^{-3}, 273 K; (d) c = 0.02 mol dm^{-3}, 263 K.



Scheme 6

from the above data. In analogy with the behaviour of 3-phenylhydrazono-4-aminopent-3-en-2-ones[1] it can be presumed that the proton of the hydrazone group in compound **1c** is bound to carbonyl by a strong intramolecular hydrogen bond (Scheme 2).

Obviously, compound **1** in $CDCl_3$ solution is present in three forms (Scheme 6): the main component is an equilibrium mixture of dimer $(\mathbf{1a})_2$ with monomer **1a**, the minor component is the isomeric monomer **1c**.



Scheme 7

Suggestion of mechanism of formation of compound 1

From the findings obtained so far it is possible to draw certain conclusions about the reaction mechanism. 4-Dimethylaminopent-3-en-2-one is attacked by the first molecule of diazonium salt at C-3 carbon atom in analogy with the β-enaminones studied so far[1–3] (Scheme 7). The subsequent reaction must be faster than primary attack by the diazonium ion: in the cases where the product of double azo coupling was formed (reactions of 4-dimethylaminopent-3-en-2-one and derivatives of 3-amino-5,5-dimethylcyclohex-2-en-1-one, ref.3), the product of this primary attack was only identified in one case (in the rection of 4-methoxybenzenediazonium with 3-amino-5,5-dimethylcyclo-hex-2-en-1-one) and was present only in traces.[3] In the cases of enaminones containing a primary or secondary amino group, the intermediate, having imonium salt characteristics, can be stabilised by splitting off of a proton. This is not possible in an enaminone with a tertiary amino group; therefore, the proton from C-5 carbon is probably split off. The intermediate that is attacked by the second diazonium ion must be enamine again since the second azo coupling reaction takes place at the carbon adjacent to the dimethylamino group and not to the carbonyl group. This stands in accord with the fact that the α-carbon atom of the enamine group is more nucleophilic that the α-carbon atom of enol.[16] Hence, the azo coupling reactions take place at different carbon atoms of the enamine skeleton, whereby they differ from the reactions of methylketones, where two subsequent azo coupling reactions take place at the same methyl group to give the corresponding formazanes,[17] and if the reactions take place at the same methylene group, they are accompanied by the Japp–Klingemann reaction.[18] The oxygen analogue of 4-dimethylaminopent-3-en-2-one, pentan-2,4-dione, only reacts with one diazonium ion at its methylene group;[19] the second coupling reaction at the methyl group was not observed, which agrees with the above-described reactivity of α-carbon atoms.

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 ^{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). 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 middle signal of the solvent multiplet (δ 77.0). The ^{15}N NMR spectra were standardised by means of external nitromethane placed in a coaxial capillary (δ 0.0). Deuteriochloroform was shaken with anhydrous sodium carbonate immediately before the measurements.

The proton signals were assigned with the help of H,H COSY pulse sequence. The signals of the minor component, which were overlapped by those of the major component, were detected by means of 1D selective TOCSY, the delay for evolution after the shaped pulse being set to 85 and 100 ms.

The nitrogen chemical shifts were measured by both direct detection and indirect detection *gs* ^{1}H–^{15}N HMBC processed in the magnitude mode. The gradient ratios were 70 : 30 : 50.1. The delay for evolution of single and multiple bond couplings was set to 10 ms and 100 ms. The values of coupling constants J (^{15}N, ^{1}H) were read either from the proton NMR spectrum of the labelled compound or from the ^{15}N INEPT spectrum measured without the proton decoupling.

The carbon NMR spectra were measured in standard way and by means of the APT pulse sequence. The assignment of the individual signals was carried out by means of 2D pulse sequences *gs* ^{1}H–^{13}C HSQC and *gs* ^{1}H–^{13}C HMBC. The HSQC pulse sequence was processed in phase sensitive mode, six transients being collected for each time increment. HMBC pulse sequence was processed in the magnitude mode.

The 2D *gs* NOESY spectra were measured with mixing time 800 ms, f_1 spectral window 5630.6 Hz with 256 data points zero filled to 512. 64 transients were collected for each time increment.

The data processing was carried out on a SGI workstation computer with Bruker microprograms.

Crystallography

The crystals for X-ray measurements were obtained by crystallisation from ethanol.

X-Ray diffraction data were collected on a Nonius Kappa CCD diffractometer with graphite monochromated Mo Kα radiation (λ = 0.7107 Å). Data sets were integrated with the Denzo-SMN package.[20] The structure was solved by direct methods (SIR92)[21] and refined (SHELXL-97)[22] by full matrix least squares with anisotropic non-H and isotropic H atoms. All other calculations were accomplished using the PARST system of programs.[23]

Pauling bond order or, more exactly, bond number, n, is simply evaluated from the formula $d(n) = d(1) - c \log n$, where $d(n)$ and $d(1)$ are the experimental and standard bond lengths, respectively. c is a constant to be evaluated for each chemical bond from standard single, $d(1)$, and double, $d(2)$ bond distances that is:

$$c = [d(1) - d(2)]/\log 2$$

The standard single and double bond distances have been taken from ref. 24.

Materials

4-Dimethylaminopent-3-en-2-one. A mixture of 0.1 mol pentan-2,4-dione and 0.2 mol aqueous solution of dimethylamine (40% solution) was stirred at room temperature for 4 h. The product was extracted with 3 × 100 ml dichloromethane, the extract was dried with anhydrous sodium sulfate and the solvent was distilled off under reduced pressure. The residue was distilled in a vacuum to give product (5.84 g, 46%); bp 85–89 °C/7 Torr (lit.[25] 125 °C/12 Torr) and mp 42–44 °C (lit.[26] 40–42 °C); δ_H(360.1 MHz; $CDCl_3$) 2.04 (3H, s, CH_3C=), 2.48 (3H, s, CH_3CO), 2.96 (6H, br s, $N(CH_3)_2$), 5.01 (1H, s, =CH–); δ_C(90.6 MHz; $CDCl_3$) 14.92 (C-5), 30.99 (C-1), 38.97 (NCH_3), 94.20 (C-3), 161.14 (C-4), 193.39 (C-2); δ_N(36.5 MHz; $CDCl_3$) −293.4.

Benzenediazonium-tetrafluoroborate. Aniline was diazotised in HCl (1 : 1) in the usual way. The reaction course was monitored by means of spot reactions on KI-starch paper, and the small excess of nitrous acid was finally removed by addition of amidosulfuric acid. The obtained solution of diazonium salt was treated with a saturated aqueous solution of $NaBF_4$. The separated benzenediazonium-tetrafluoroborate was collected by suction, washed with cold methanol and several times with ether, and dried in a desiccator. If kept in a refrigerator, the product is stable over several months.

(^{15}N)-Benzenediazonium-tetrafluoroborate. The diazotisation was carried out in HBF_4 (*ca.* 8.4 mol dm^{-3}) using (^{15}N)-aniline and/or (^{15}N)-$NaNO_2$ of various degrees of isotope enrichment. The diazonium salt was isolated in the same way as described above for the isotopically non-labelled compound.

4-Dimethylamino-5-(phenyldiazenyl)pent-4-en-2,3-dione 3-phenylhydrazone 1. A solution of 0.5 g (3.9 mmol) 4-dimethylaminopent-3-en-2-one in 15 ml diisopropyl ether was stirred and treated with 1.6 g (19.5 mmol) melted, finely ground sodium acetate and 1.5 g (7.8 mmol) benzenediazonium-tetrafluoroborate. The mixture was stirred at room temperature for 3 h. The solid portion was collected by suction and extracted with 3 × 10 ml dry dichloromethane. The solvent was distilled off in a vacuum at room temperature. The evaporation residue was recrystallised from dry methanol to give red crystalline solid (0.35 g, 26.8%); mp 161–163 °C with decomposition. (Found C 68.11; H 6.34; N 21.04. $C_{19}H_{21}N_5O$ requires C 68.04; H 6.31; N 20.88%).

4-Dimethylamino-5-[$^{15}N_2$]-(phenyldiazenyl)pent-4-en-2,3-dione 3-[$^{15}N_2$]-phenylhydrazone. The compound was prepared in the same way as described above for the isotopically non-labelled compound. Mp 165–168 °C.

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References

1 V. Macháček, A. Lyčka, P. Šimůnek and T. Weidlich, *Magn. Reson. Chem.*, 2000, **38**, 293–300.
2 P. Šimůnek, V. Bertolasi and V. Macháček, *J. Mol. Struct.*, 2002, **642**, 41–51.
3 P. Šimůnek, A. Lyčka and V. Macháček, *Eur. J. Org. Chem.*, 2002, 2764–2769.
4 V. Macháček, A. Čegan, A. Halama and O. Rožňavská, *Collect. Czech. Chem. Commun.*, 1995, **60**, 1367–1379.
5 S. Al-Mousawi, M. M. Abdel-Khalik, S. El-Sherbiny, E. John and M. H. Elnagdi, *J. Heterocycl. Chem.*, 2001, **38**, 949–953.
6 C. K. Johnson, ORTEP-II: A FORTRAN Thermal Ellipsoid Plot Program for Crystal Structure Illustrations, Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN, USA, 1976.
7 L. Pauling, *J. Am. Chem. Soc.*, 1947, **69**, 542–553.
8 V. Bertolasi, P. Gilli, V. Ferretti, G. Gilli, K. Vaughan and J. Jollimore, *Acta Crystallogr., Sect. B: Struct. Sci.*, 1999, **55**, 994–1004.
9 V. Ferretti, V. Bertolasi, P. Gilli and G. Gilli, *J. Phys. Chem.*, 1993, **97**, 13568–13574.
10 L. Llamas Saiz and C. Foces-Foces, *J. Mol. Struct.*, 1990, **238**, 367–382.
11 A. Lyčka, D. Šnobl, V. Macháček and M. Večeřa, *Org. Magn. Reson.*, 1981, **16**, 17–19.
12 R. Marek and A. Lyčka, *Curr. Org. Chem.*, 2002, **6**, 35–66.
13 A. Lyčka, *Annu. Rep. NMR Spectrosc.*, 1993, **26**, 247–281.
14 A. Lyčka A., *Annu. Rep. NMR Spectrosc.*, 2000, **42**, 1–57.
15 K. Kamieńska-Trela, L. Kania, J. Sitkowski and L. Kaczmarek, *J. Chem. Soc., Perkin Trans. 2*, 1995, 1617–1624.
16 F. A. Carey and F. A. Sundberg, *Advanced Organic Chemistry*, Part A, Plenum Press, New York, 3rd edn., 1990, p. 422.
17 V. Macháček, O. Macháčková and V. Štěrba, *Collect. Czech. Chem. Commun.*, 1970, **35**, 2954–2964.
18 R. R. Phillips, *Org. React.*, 1959, **10**, 143–178.
19 V. Macháček, J. Panchartek and V. Štěrba, *Collect. Czech. Chem. Commun.*, 1970, **35**, 3410–3419.
20 Z. Otwinowski and W. Minor, in *Methods in Enzymology*, ed. C. W. Carter and R. M. Sweet, Academic Press, London, 1997, Vol. 276, Part A, p. 307.
21 A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M. C. Burla, C. Polidori and M. Camalli, *J. Appl. Crystallogr.*, 1994, **27**, 435–435.
22 G. M. Sheldrick, SHELXL-97, Program for refinement of crystal structures, University of Göttingen, Germany, 1997.
23 M. Nardelli, *J. Appl. Crystallogr.*, 1995, **28**, 659–659.
24 *Tables of Bond lengths Determined by X-Ray and Neutron Diffraction. Part 1. Bond lengths in Organic Compounds*. F. H. Allen, O. Kennard, D. G. Watson, L. Brammer, A. G. Orpen and R. Taylor, *J. Chem. Soc. Perkin Trans. 2*, 1987, S1–S19.
25 K. F. W. Kolrausch and A. Pongratz, *Monatsh. Chem.*, 1937, **70**, 226–235.
26 Zu. Safina, G. Sh. Malkova and R. A. Cherkasov, *Zh. Obshch. Khim.*, 1991, **61**, 620–634.