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^{13}C- and ^{15}N-NMR Spectra of Phenylazoacetoacetamides and Similar Compounds

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SUMMARY

*The ^{13}C- and ^{15}N-NMR spectra of phenylazoacetoacetamides (**1**) and similar compounds and their ^{15}N-isotopomers have been measured and the carbon and nitrogen signals have been assigned. The compounds exist in their hydrazone forms. Based on the stereospecific behaviour of the coupling constants $^2J(^{15}N^{13}C)$ a strong predominance of (Z)-isomer has been found for the compounds **1** in C^2HCl_3 or in $[^2H_6]$DMSO solutions. In some cases (E)-isomers ($\leq 5\%$) have been observed.*

1. INTRODUCTION

The coupling of diazonium salts with β-ketoanilides has been studied extensively because the products have found use as yellow dyes and pigments.[1] The coupling products may be formulated as existing in both hydrazone and azo tautomeric forms; Kettrup *et al.*[2] have collected the possible structural formulae for these compounds (Scheme 1). The structure of **H3** has been suggested in ref. 3. Much of the early work with the above-mentioned coupling reaction was prompted by the desire to determine whether the products were of the azo or hydrazone structure.[1] It was generally assumed that the hydrazones are the stable forms[1–5] but Yagi[4,5] has preferred (*E*)-isomers (**H2**), Kettrup *et al.*[2] (*Z*)-isomers (**H1**) and Dyumaev *et al.*[3] have suggested a configuration denoted as **H3**.

The aim of this present study was to measure the ^{13}C- and ^{15}N-NMR spectra of the azo coupling products of substituted benzenediazonium

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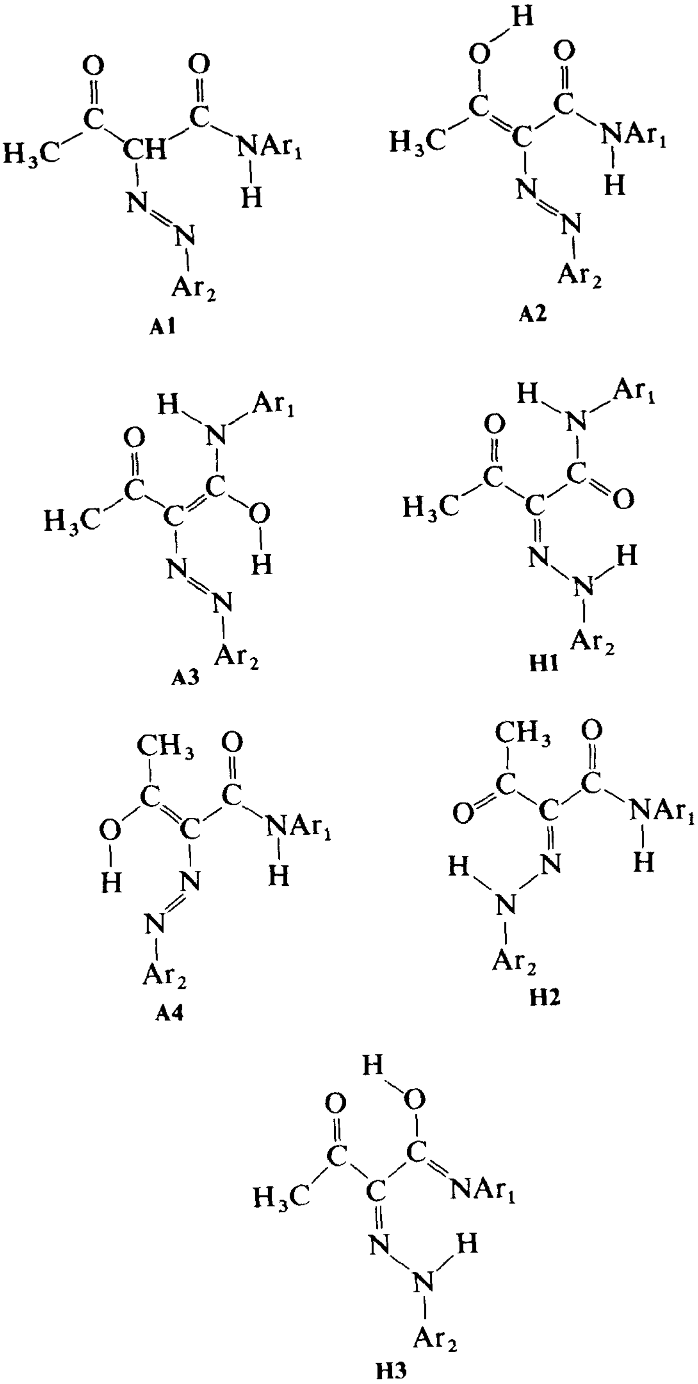
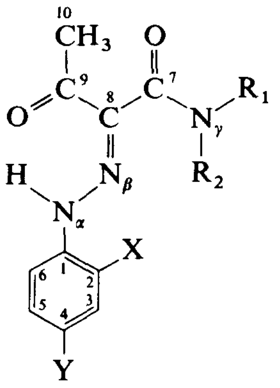


Scheme 1

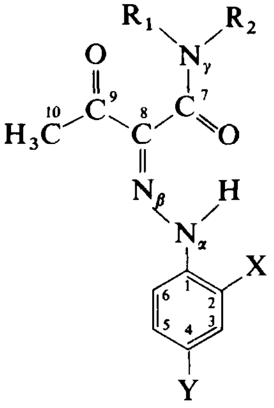
chlorides with acetoacetamides (**1**) and malonodiamides (**2**) as well as of the respective ^{15}N-isotopomers and to use the ^{13}C- and ^{15}N-NMR characteristics for estimation of the *E*/*Z* isomer ratio in the compounds **1**.

2. EXPERIMENTAL

The compounds **1a**–**1f** and **2a**,**2b** (Scheme 2) were prepared by known methods.[1] Their ^{15}N-isotopomers (N_α, 15% ^{15}N; N_β, 95% ^{15}N) were

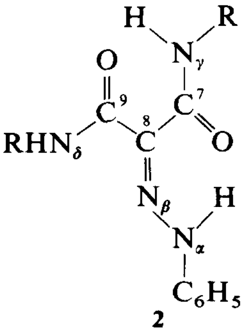


(*E*)-**1**



(*Z*)-**1**

	R_1	R_2	X	Y
1a	H	H	H	H
1b	H	C_6H_5	H	H
1c	H	C_6H_5	H	NO_2
1d	CH_3	CH_3	H	H
1e	CH_3	C_6H_5	H	H
1f	H	C_6H_5	OH	H



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2a: R = H
2b: R = CH_3

Scheme 2

prepared in the same way using $Na^{15}NO_2$ and $C_6H_5{}^{15}NH_2$ (Isocommerz, Berlin). $[^2H_5]$Benzenediazonium chloride was used for the preparation of $[^2H_5]$**1b**. 2-Amino-$[3,5\text{-}^2H_2]$phenol for the preparation of $[^2H_2]$**1f** was obtained from 2-aminophenol (3 g) by boiling in the mixture of 3 ml conc. HCl and 50 ml ^2H_2O. After approximately 20 h the mixture was neutralized and the product was collected. Deuterium content (about 85% in positions 3 and 5) was checked indirectly using ^{1}H-NMR.

The ^{13}C-, ^{15}N- and ^{1}H-NMR spectra were measured at 25·047, 10·095 and 99·602 MHz, respectively, using a JNM-FX 100 (JEOL) spectrometer equipped with a multinuclear tunable probe and operating in the FT mode. The spectra were recorded for *ca.* 20% (w/v) solutions in deuteriochloroform or hexadeuteriodimethyl sulfoxide at 300 K. The deuterated solvents were used as lock substances. The measurement conditions are given in ref. 6 For the measurement of some ^{15}N chemical shifts, the solutions were treated with chromium tris(acetylacetonate) (about 10 mg/ml). The ^{13}C chemical shifts were referred to the signal of C^2HCl_3 ($\delta = 77{\cdot}0$) or $[^2H_6]$DMSO ($\delta = 39{\cdot}6$) and the ^{15}N chemical shifts were related to external nitromethane (25% ^{15}N; $\delta = 0{\cdot}0$). The chemical shifts were determined with an accuracy better than 0·2 ppm and all coupling constants with an accuracy better than 0·3 Hz.

3. RESULTS AND DISCUSSION

The values of the ^{13}C and ^{15}N chemical shifts and absolute values of the coupling constants $^1J(^{15}N^{15}N)$, $^nJ(^{15}N_\beta{}^{13}C)$ and $^nJ(^{15}NH)$ of the compounds **1a–1f** and **2a,2b** are given in Tables 1 and 2, respectively.

Only one set of signals was observed in the ^{13}C-NMR spectra of **1** and **2**. The carbon chemical shifts of the phenyl groups were assigned according to the typical pattern of the proton-decoupled and coupled spectra of monosubstituted benzene. In compound **1b** two phenyl groups were distinguished using the pentadeuterated compound **1b** (see Section 2) and, similarly, the signals of C(4) and C(6) were assigned on the basis of the ^{13}C-NMR spectrum of the doubly deuterated compound **1f**. In ^{2}H-isotopomers, the $\underline{C}\text{-}^2H$ signals were split into triplets and the relative intensity of the C(1) signal decreased to *ca.* one-fifth of its original value as the result of the change in the relaxation mechanism.[7] The $\underline{C}O$ groups absorb at the lowest field. The other ^{13}C signals were assigned after inspection of the proton-coupled spectra and in some cases $^n(^{15}N_\beta{}^{13}C)$ were also used.

The C(8) signals absorb in the aromatic region of ^{13}C-NMR spectra and correspond to quaternary carbon. From this fact it follows that

TABLE 1

^{13}C Chemical Shifts and Coupling Constants $^{n}J(^{15}N_{\beta}{}^{13}C)$ (in Parentheses) of Compounds **1a**–**1f** and **2a**,**2b** in Deuteriochloroform at 300 K

Compound	Carbon number									
	1	*2*	*3*	*4*	*5*	*6*	*7*	*8*	*9*	*10*
1a	141·6	115·8	129·5	125·2	129·5	115·8	166·6	126·0	198·5	25·9
	(6·1)	(2·6)				(2·6)	(0·7)	(3·8)	(13·2)	(1·2)
1b[a]	141·3	115·4	129·1	124·9	129·1	115·4	162·4	125·3	198·9	25·6
	(6·4)	(2·2)				(2·2)	(1·1)	(4·0)	(13·2)	(1·1)
1b[b]	141·5	[c]	[c]	[c]	[c]	[c]	162·8	126·0	199·2	25·9
1c[d]	146·6	115·4	125·8	144·2	125·8	115·4	162·2	128·5	199·7	26·3
1d[e]	142·1	114·7	129·4	123·5	129·4	114·7	163·2	135·7	194·7	24·6
	(6·1)	(2·1)				(2·1)	(1·2)	(4·3)	(12·2)	
1e[f]	142·3	114·5	129·0[g]	122·8	129·0[g]	114·5	163·9	136·5	194·3	23·8
	(6·1)	(2·0)				(2·0)	(1·1)	(4·0)	(12·1)	
1f[h,i]	129·7	146·8	116·0	125·9	120·0	114·6	162·3	125·9	198·8	26·0
	(5·9)						(<0·8)		(13·2)	
1f[j]	129·9	147·1	116·1	[c]	120·2	[c]	162·6	126·2	199·0	26·3
2a[h]	142·0	115·1	129·3	123·6	129·3	115·1	166·1	120·4	167·4	
	(6·3)	(2·0)				(2·0)	(1·2)	(4·5)	(10·6)	
2b[k]	141·9	114·8	129·4	123·7	129·4	114·8	165·3	119·7	166·0	

[a] $\delta(NH\underline{C}_6H_5) = 136{\cdot}9(C_i);\ 120{\cdot}2(C_o);\ 128{\cdot}0(C_m);\ 124{\cdot}2(C_p)$.

[b] Coupling product with $C_6{}^2H_5NH_2$. $\delta(NH\underline{C}_6H_5) = 137{\cdot}1(C_i);\ 120{\cdot}7(C_o);\ 128{\cdot}9(C_m);\ 124{\cdot}6(C_p)$.

[c] Badly resolved triplet of C—^2H.

[d] $\delta(NH\underline{C}_6H_5) = 136{\cdot}6(C_i);\ 121{\cdot}0(C_o);\ 129{\cdot}1(C_m);\ 125{\cdot}3(C_p)$.

[e] $\delta(N\underline{C}H_3) = 38{\cdot}2$ and $34{\cdot}6$.

[f] $\delta(NH\underline{C}_6H_5) = 141{\cdot}5(C_i);\ 125{\cdot}6(C_o);\ 128{\cdot}9^{g}(C_m);\ 127{\cdot}8(C_p);\ \delta(N\underline{C}H_3) = 36{\cdot}3$.

[g] Assignment may be reversed.

[h] Measured in $[^2H_6]$DMSO.

[i] $\delta(NH\underline{C}_6H_5) = 137{\cdot}3(C_i);\ 120{\cdot}4(C_o);\ 129{\cdot}2(C_m);\ 124{\cdot}5(C_p)$.

[j] Coupling product with 2-amino-$[3,5\text{-}^2H_2]$phenol; $\delta(NHC_6H_5) = 137{\cdot}5(C_i);\ 120{\cdot}6(C_o);\ 129{\cdot}4(C_m);\ 124{\cdot}8(C_p)$.

[k] $\delta(N\underline{C}H_3) = 26{\cdot}0$ and $25{\cdot}1$.

C_{i-p} = ipso-C, ortho-C, meta-C, para-C.

TABLE 2

^{15}N Chemical Shifts and Coupling Constants $^{n}J(^{15}\mathrm{NX})$ in Compounds **1a**–**1f** and **2a** in Deuteriochloroform at 300 K

Compound	$\delta(^{15}N)$				$^{1}J(^{15}N_\alpha{}^{15}N_\beta)$	$^{1}J(^{15}N_\alpha H)$	$^{2}J(^{15}N_\beta H)$
	N_α	N_β	N_γ	N_δ			
1a	$-201{\cdot}6^{a}$	$1{\cdot}0^{a}$	$-274{\cdot}5^{b}$	—	$10{\cdot}5^{a}$	$95{\cdot}4^{a}$	$2{\cdot}4^{a}$
1a^{c}	$-204{\cdot}6^{b}$	$-2{\cdot}4^{b}$	$-270{\cdot}3^{b}$	—	—	—	—
1b	$-201{\cdot}3^{a}$	$0{\cdot}4^{a}$	$-245{\cdot}6^{b}$	—	$10{\cdot}9^{a}$	$95{\cdot}3^{a}$	$2{\cdot}3^{a}$
1d	$-224{\cdot}9^{a}$	$-27{\cdot}6^{a}$	^{d}	—	$10{\cdot}9^{a}$	$94{\cdot}8^{a}$	$2{\cdot}7^{a}$
1e	$-227{\cdot}2^{a}$	$-30{\cdot}1^{a}$	^{d}	—	$11{\cdot}0^{a}$	$94{\cdot}6^{a}$	$2{\cdot}2^{a}$
1f^{c}	$-206{\cdot}7^{b,e}$	$-4{\cdot}1^{f}$	$-246{\cdot}0^{b,e}$	—	—	—	—
2a^{c}	$-213{\cdot}7^{a}$	$-20{\cdot}3^{a}$	$-269{\cdot}1^{b}$	$-281{\cdot}0^{b}$	$10{\cdot}7^{a}$	$95{\cdot}2^{a}$	$2{\cdot}2^{a}$

[a] ^{15}N-doubly labelled compound.

[b] Measured at ^{15}N natural abundance level.

[c] Measured in [$^{2}H_6$]DMSO.

[d] Not found even when chromium tris(acetonylacetate) as relaxation reagent had been added.

[e] Measured at 330 K.

[f] ^{15}N-monolabelled compound.

compounds **1** and **2** exist as hydrazone compounds and the existence of *E*/*Z* isomerism on the $N_\beta{=}C(8)$ double bond can be expected in **1**. The coupling constants $^2J(^{15}N^{13}C)$ are known to be stereospecific.[8,9] The carbon atom at the *cis* position with respect to the free electron pair at the nitrogen atom has a coupling constant markedly greater (usually ~10 Hz) than that in the *trans* position (~1 Hz). We have prepared ^{15}N-labelled compounds **1** and **2**; in their ^{13}C-NMR spectra the signals for $CH_3\underline{C}O$ were split with much greater $^2J(^{15}N_\beta{}^{13}C)$ than those for $\underline{C}ONR_1R_2$ in **1** and $\underline{C}ONR_1R_2$ in **2** were distinguished in the same way (Table 1). Thus, the compounds **1** exist predominantly (see below) as (*Z*)-isomers. (*Z*)-Isomers are stabilized by the formation of the second hydrogen bond in compounds **1a**–**1c**,**1f** ($R_1 = H$) but the formation of this second hydrogen bond does not play any decisive role because (*Z*)-isomers were also found in compounds **1d**,**1e** ($R = CH_3$) where the second hydrogen bond cannot exist.

^{15}N chemical shifts of compounds **1** and **2** were measured using ^{15}N-doubly labelled compounds (N_α, 15% ^{15}N; N_β, 95% ^{15}N). Different values of the ^{15}N enrichment enable us to measure $\delta(^{15}N_\alpha)$ and $\delta(^{15}N_\beta)$ very quickly (and to assign them unambiguously when necessary), to measure $^nJ(^{15}NH)$, $^1J(^{15}N_\alpha{}^{15}N_\beta)$ and $^nJ(^{15}N_\beta{}^{13}C)$ (from ^{13}C-NMR spectra), all in one sample. Both ^{15}N chemical shifts and appropriate coupling constants correspond to the typical values of hydrazone compounds.[6,10–13] The ^{15}N chemical shifts of N_γ and N_δ in **2a** were assigned after comparison with $\delta(N_\gamma)$ in compound **1a** measured in [$^2H_6$]DMSO.

^{15}N-labelling enables us to assign ^{1}H-NMR signals of $-N_\alpha\underline{H}N{=}$ because of splitting of the ^{1}H signal into a doublet due to $^1J(^{15}NH)$ (**1a**, $\delta = 14{\cdot}6$; **1b**, $\delta = 14{\cdot}7$; **1c**, $\delta = 14{\cdot}9$; **1d**, $\delta = 10{\cdot}0$; **1e**, $\delta = 10{\cdot}0$ (all in C^2HCl_3); **1f**, $\delta = 14{\cdot}5$; **2a**, $\delta = 14{\cdot}2$ (both in [$^2H_6$]DMSO). The second hydrogen bond formation in compounds **1a**–**1c**, **1f** and **2a** causes approximately 4·2–4·9 ppm downfield shifts of $\delta(-N_\alpha\underline{H}N{=})$ in comparison with $\delta(-N_\alpha\underline{H}N{=})$ in compounds **1d**,**e**. This is an important finding because $\delta(-N_\alpha\underline{H}N{=}) \sim 14{\cdot}5$ could lead to a mistaken interpretation of *E*/*Z* isomerism in compounds **1** from ^{1}H-NMR spectra only after comparison with, e.g., $\delta(-N_\alpha\underline{H}N{=}) = 14{\cdot}68$ in pentane-2,3,4-trione 3-phenylhydrazone[6] or $\delta(-N_\alpha\underline{H}N{=}) = 14{\cdot}83$ in (*E*)-ethyl 2-phenylhydrazono-3-oxobutanoate[6] having a hydrogen bond to CH_3CO- groups. Protons of the CONHR groups in the second hydrogen bonds absorb within the range 9·1–11·5 ppm and so the previous assignment of δ(NH) in the above-mentioned two hydrogen bonds must be interchanged in Table 7 in ref. 2.

^{1}H-NMR spectroscopy is much more sensitive[14] than ^{13}C- and ^{15}N-NMR spectroscopy. In the ^{1}H-NMR spectra of **1d** and **1e** we have observed weak signals ($\leq 5\%$) of $-N_\alpha\underline{H}N{=}$ groups at 14·0 and 13·8, respectively, and appropriate signals of $C\underline{H}_3CO-$ groups which should correspond to (*E*)-isomers.

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