

**^{13}C AND ^{15}N -NMR STUDIES
OF 2,3,4-PENTANETRIONE 3-PHENYLHYDRAZONE,
DIMETHYL 2-PHENYLHYDRAZONOPROPANEDIOATE
AND ETHYL 2-PHENYLHYDRAZONO-3-OXOBUTANOATE**

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The ^{13}C and ^{15}N -NMR spectra of 2,3,4-pentanetrione 3-phenylhydrazone, dimethyl 2-phenylhydrazonopropanedioate and ethyl 2-phenylhydrazono-3-oxobutanoate have been measured in deuteriochloroform at 30°C. The carbon and nitrogen signals have been assigned, and the chemical shifts and coupling constants $^1J(\text{CH})$ have been determined. Ethyl 2-phenylhydrazono-3-oxobutanoate has been measured first as the (*E*) isomer and then as a mixture of the (*E*) and (*Z*) isomers. This compound has also been prepared with one or two ^{15}N atoms enabling determination of absolute values of the coupling constants $^nJ(^{15}\text{N}^{13}\text{C})$ and $^1J(^{15}\text{N}^{15}\text{N})$, respectively.

Coupling products of benzenediazonium salts with methylene group of 1,3-diketones and 3-ketoesters have been studied so far by means of ^1H -NMR, IR and electron spectroscopies. Yao¹ observed two ^1H -NMR signals for the COCH_3 groups of 2,3,4-pentanetrione 3-phenylhydrazone, The chemical shift of the NH group was 14.68 ppm, which corresponds to a hydrogen bridge to one carbonyl group. Ethyl 2-phenylhydrazono-3-oxobutanoate² exists as two geometrical isomers in deuteriochloroform ($\delta(\text{NH}) = 14.83$ and 12.61). Existence of hydrazo forms of these compounds was proved unambiguously by measurements of the coupling constant $^1J(^{15}\text{N}^1\text{H})$ of the suitably ^{15}N -labelled compounds by means of ^1H -NMR (refs²⁻⁴). Absolute values of these coupling constants are within 94.7 to 96.1 Hz and are typical of hydrazo compounds⁵. Characterization of geometrical isomers of arylhydrazones of triketones and substituted diketones by means of ^1H -NMR, IR and electron spectroscopies is given in a report⁶ by Courtot and coworkers. The same authors described photochromism of such compounds due to isomerization⁷. The aim of this work is to characterize 2,3,4-pentanetrione 3-phenylhydrazone (*I*), dimethyl 2-phenylhydrazonopropanedioate (*II*) and ethyl 2-phenylhydrazono-3-oxobutanoate (*III*) by means of ^{13}C and ^{15}N -NMR spectra.

EXPERIMENTAL

2,3,4-Pentanetrione 3-phenylhydrazone¹ (*I*), dimethyl 2-phenylhydrazonopropanedioate⁸ (*II*) and ethyl 2-phenylhydrazono-3-oxobutanoate⁸ (*III*) were prepared according to literature. The ^{15}N -labelled compounds *III* were prepared from ^{15}N -labelled aniline (94.8% ^{15}N) and $\text{Na}^{15}\text{NO}_2$ (96.2% ^{15}N) (Isocommerz, Berlin).

The ^{13}C and ^{15}N spectra were measured at 25.047 and 10.095 MHz, respectively, using a JNM-FX 100 apparatus (JEOL) equipped with a multinuclear tunable probe, quadrature

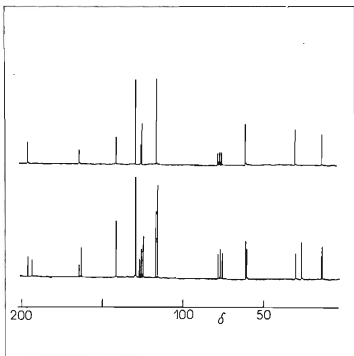


FIG. 1

^{13}C -NMR Spectra of (*E*)-Ethyl 2-Phenylhydrazono-3-oxobutanoate (top) and of Mixture (*E*) and (*Z*)-Ethyl 2-Phenylhydrazono-3-oxobutanoate in Deuteriochloroform

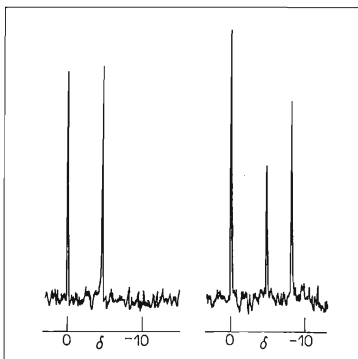


FIG. 2

^{15}N -NMR Spectra of (*E*)-Ethyl 2-Phenylhydrazono-3-oxobutanoate (left) and of Mixture (*E*) and (*Z*)-Ethyl 2-Phenylhydrazono-3-oxobutanoate in Deuteriochloroform for N_β

detection, and working in the FT mode. The spectra were recorded for 25% (w/v) solutions of the compounds *I*, *II* and (*E*) isomer of *III* in deuteriochloroform at 30°C. The (*Z*) isomer of *III* was measured in a mixture with (*E*)-*III* in the ratio 3 : 2. The ^{15}N -labelled compounds *III* were measured as 3–5% (w/v) solutions. The measured solutions were placed in 10 mm NMR test tubes, and deuteriochloroform was used as lock. The carbon chemical shifts were referred to internal tetramethylsilane, and the ^{15}N chemical shifts were referred to external neat nitromethane⁹ (25% ^{15}N). The following parameters were used to obtain the ^{13}C chemical shifts: spectral width 5000 Hz, 16 k memory, pulse width 7 μs (23 μs $\sim 90^\circ$), pulse repetition 3 s, the proton noise decoupling; for obtaining $^1\text{J}(\text{CH})$ the same parameters were used but with pulse repetition of 6 s and gated decoupling. Values of the coupling constants $^n\text{J}(^{15}\text{N}^{13}\text{C})$ were measured with the ^{15}N -monolabelled compounds using the digital resolution of 0.26 Hz/point and the proton noise decoupling. For obtaining the ^{15}N chemical shifts the following parameters were used: for $-\text{N}=\text{C}$ spectral width 4000 Hz, 8 k memory, pulse width 7 μs (30 μs $\sim 90^\circ$), pulse repetition 30 s, inverse gated decoupling¹⁰ (the proton noise decoupling during the period of the signal acquisition); for $-\text{NH}-$ spectral width 4000 Hz, 8 k memory, pulse width 7 μs , pulse repetition 5 s, the proton noise decoupling. The $^1\text{J}(^{15}\text{N}^{15}\text{N})$ coupling constants were measured with the digital resolution 0.1 Hz/point and with the proton noise decoupling (Figs 1 and 2).

RESULTS AND DISCUSSION

The proton chemical shift of NH group in 2,3,4-pentanetrione 3-phenylhydrazone (*I*) is 14.68 ppm (ref.¹), with diethyl 2-phenylhydrazonopropanedioate (*II*) the shift of the same group being 12.8 ppm. Bose and Kugajevsky² observed two chemical shifts of NH group with the ^{15}N -labelled 2-phenylhydrazono-3-oxobutanoate (*III*) (14.83 and 12.61 ppm) with the signals split by ^{15}N into doublets ($|^1\text{J}(^{15}\text{N}^1\text{H})| =$

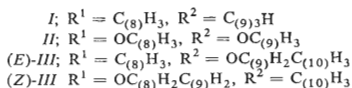
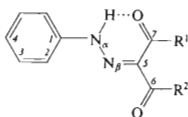
TABLE I
 ^{13}C Chemical Shifts (δ Scale, ± 0.05 ppm) of the Compounds *I*–*III* in Deuteriochloroform

Carbon	<i>I</i>	<i>II</i>	(<i>E</i>)- <i>III</i>	(<i>Z</i>)- <i>III</i>
1	141.30	141.35	141.38	141.38
2	115.98	115.42	116.15	115.18
3	129.38	129.18	129.19	129.24
4	125.61	124.61	125.44	124.56
5	132.94	118.64	125.68	126.75
6	196.63	163.59	164.69	163.40
7	197.53	163.35	196.63	193.93
8	31.44	51.98 ^a	30.54	60.97
9	26.39	51.85 ^a	60.65	13.85
10	—	—	14.16	26.52

^a The assignment can be opposite.

= 94.7 and 96.1 Hz) which were not univocally assigned. From comparison it follows that the signal at lower field and $^1J(^{15}\text{N}^1\text{H}) = 94.7$ Hz corresponds to the (*E*) isomer. The coupling product from benzenediazonium chloride and ethyl 3-oxobutanoate, precipitated almost immediately after addition of the diazonium salt and subsequently water, was measured by ^1H -NMR in deuteriochloroform. The spectrum only contained the absorption at 14.8 ppm corresponding to the (*E*)-*III* isomer. On standing for several days at room temperature this solution gave a mixture of (*E*)-*III* and (*Z*)-*III* (about 2 : 3). The remaining coupling product isolated after 24 h contained 10–15% (*Z*)-*III* isomer.

The ^{13}C chemical shifts of the compounds *I–III* are given in Table I. The carbon chemical shifts of the phenyl group were assigned according to the typical pattern of decoupled and coupled spectra of monosubstituted phenyl group. The assignment of the ^{13}C chemical shifts of CO and alkyl groups was carried out by mutual comparison. After isomerization of (*E*)-*III* to a mixture of (*E*)-*III* and (*Z*)-*III* the chemical



shifts of carbonyl and ester groups of (*Z*)-*III* were shifted downfield, those of methylene group being shifted upfield. This presumption allowed to assign the ^{13}C chemical shifts of carbonyl carbons and carbons of methylene groups of the compound *I*

TABLE II
Coupling Constants $^1J(\text{CH})$ (Hz) of the Compounds *I–III* in Deuteriochloroform

Compound	$\text{C}_{(2)}^a$	$\text{C}_{(3)}^a$	$\text{C}_{(4)}^a$	$\text{C}_{(8)}^b$	$\text{C}_{(9)}^b$	$\text{C}_{(10)}^b$
<i>I</i>	161.2	161.2	162.5	129.0	128.2	—
<i>II</i>	161.0	160.6	161.5	147.1	148.1	—
(<i>E</i>)- <i>III</i>	161.9	161.7	162.4	129.0	147.1	127.0
(<i>Z</i>)- <i>III</i>	161.9	161.7	162.4	128.4	148.3	127.2

^a ± 0.9 Hz; ^b ± 0.4 Hz.

and those of ester and methoxy carbons of *II*. The coupling constants $^1J(\text{CH})$ are given in Table II. The ^{15}N -labelled compounds were prepared for determination of the coupling constants $^nJ(^{15}\text{N}^{13}\text{C})$. Ethyl 2-phenylhydrazono-3-oxobutanoate was chosen, because it contains both carbonyl and ester groups both free and hydrogen-bonded. Absolute values of the coupling constants $^nJ(^{15}\text{N}^{13}\text{C})$ (Table III) of carbons of phenyl nucleus and $\text{C}(5)$ are the same for both (*E*)-*III* and (*Z*)-*III* within experimental error. The values of $^nJ(^{15}\text{N}^{13}\text{C})$ of $\text{C}_{(8)}-\text{C}_{(10)}$ are less than 0.5 Hz. Absolute values of the coupling constants $^3J(^{15}\text{N}^{13}\text{C})$ of the carbons $\text{C}_{(7)}$ are always less than those of $\text{C}_{(6)}$ in contrast to the coupling constants of the geometrically corresponding positions $^3J(^{15}\text{N}^{13}\text{C}_{(4)})$ of pyridine¹¹ (3.85 Hz) and $^3J(^{15}\text{N}^{13}\text{C}_{(5)})$ of quinoline¹² (~ 0 Hz). $^2J(^{15}\text{N}^{13}\text{C})$ of $\text{C}_{(7)}$ are substantially less than those of $\text{C}_{(6)}$, which corresponds to the interactions in the compounds type *IV* (ref.¹³)

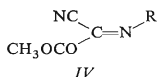


TABLE III
Absolute Values of Coupling Constants $^nJ(^{15}\text{N}^{13}\text{C})$ (Hz, ± 0.3 Hz) of the ^{15}N -Monolabelled Compounds (*E*)-*III* and (*Z*)-*III* in Deuteriochloroform

Compound	Labelled atom	$\text{C}_{(1)}$	$\text{C}_{(2)}$	$\text{C}_{(3)}$	$\text{C}_{(4)}$	$\text{C}_{(5)}$	$\text{C}_{(6)}$	$\text{C}_{(7)}$
(<i>E</i>)- <i>III</i>	N_β	6.6 ^b	2.4 ^c	<0.3 ^d	<0.3 ^e	3.4 ^a	0.3 ^b	10.5 ^b
(<i>Z</i>)- <i>III</i>	N_β	6.6 ^b	2.4 ^c	<0.3 ^d	<0.3 ^e	3.7 ^e	1.0 ^b	12.6 ^b
(<i>E</i>)- <i>III</i>	N_α	18.7 ^a	2.0 ^b	2.1 ^c	0.3 ^d	1.3 ^b	1.0 ^c	3.4 ^c
(<i>Z</i>)- <i>III</i>	N_α	19.7 ^a	2.0 ^b	2.1 ^c	0.3 ^d	1.3 ^b	0.9 ^c	3.7 ^c

^a 1 J ; ^b 2 J ; ^c 3 J ; ^d 4 J ; ^e 5 J .

TABLE IV
 ^{15}N Chemical Shifts (± 0.1 ppm) Referred to External Neat Nitromethane (25% ^{15}N) for the Compounds *I*-*III* in Deuteriochloroform

Compound	<i>I</i>	<i>II</i>	(<i>E</i>)- <i>III</i>	(<i>Z</i>)- <i>III</i>
$\delta(\text{N}_\beta)$	— 5.4	— 8.5	— 5.1	— 8.8
$\delta(\text{N}_\alpha)$	— 203.7	— 209.4	— 202.1	210.9

where $^2J(^{15}\text{N}^{13}\text{CN}) \sim 1-2.2$ Hz and $^2J(^{15}\text{N}^{13}\text{COOCH}_3) \sim 10.5$ Hz, Hence the values of $^2J(^{15}\text{N}^{13}\text{C})$ agree with the assignment of the carbon signals of the (E) and (Z) geometrical isomers of the compound III.

Values of the ^{15}N chemical shifts (Table IV) were obtained at the natural abundance level of the ^{15}N isotope. The upfield shifts are taken as negative. The assignment corresponds to characteristic difference of chemical shifts of the groups $-\text{N}=\text{N}-$ and $-\text{NH}-$ (ref.¹⁴), and it was confirmed by measurement of the ^{15}N -monolabelled compounds III which were used for determination of $^nJ(^{15}\text{N}^{13}\text{C})$. The influence of five- to eight-fold dilution is small ($\delta((E)\text{-III}) = -4.8, -202.2$; $\delta((Z)\text{-III}) = -8.2, -211.1$; see Table IV). The both ^{15}N chemical shifts of the compounds having a hydrogen bond to the ester carbonyl group (II and (E)-III) are shifted upfield as compared with the nitrogen shifts of the compounds having a hydrogen bond to acetyl carbonyl group (I and (E)-III). Compared with phenylhydrazones of aromatic aldehydes¹⁵ the ^{15}N chemical shifts of the compounds I-III are shifted downfield, this trend being more marked for $\text{N}\beta$. With the ^{15}N -double-labelled compound III the following values of coupling constant $^1J(^{15}\text{N}^{15}\text{N})$ were found: 11.1 ± 0.1 and 10.8 ± 0.1 Hz for (E)-III and (Z)-III, respectively. Thus the value of $^1J(^{15}\text{N}^{15}\text{N})$ of (E)-III is greater than that of (Z)-III in contrast to the value $^1J(^{15}\text{N}^1\text{H})$ which shows an opposite trend.

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REFERENCES

1. Yao H. C.: J. Org. Chem. 29, 2959 (1964).
2. Bose A. K., Kugajevsky I.: Tetrahedron 23, 1489 (1967).
3. Reichard C., Grahn W.: Chem. Ber. 103, 1065 (1970).
4. Reichard C., Grahn W.: Tetrahedron 27, 3745 (1971).
5. Axenrod T. in the book: Nitrogen NMR (M. Witanowski, G. A. Webb, Eds), p. 261. Plenum Press, London 1973.
6. Courtot P., Pichon R., LeSaint J.: Tetrahedron Lett. 1976, 1177.
7. Courtot P., Pichon R., LeSaint J.: Tetrahedron Lett. 1976, 1181.
8. Bülow C., Neber P.: Chem. Ber. 45, 3736 (1912).
9. Witanowski M., Stefaniak L., Szymanski S., Januszewski H.: J. Magn. Resonance 28, 217 (1977).
10. Hawkes G. E., Randall E. W., Hull W. E.: J. Chem. Soc., Perkin Trans. 2, 1977, 1268.
11. Bundgaard T., Jakobsen H. J.: Tetrahedron Lett. 1976, 1621.
12. Pregosin P. S., Randall E. W., White A. I.: J. Chem. Soc., Perkin Trans. 2, 1972, 1.
13. Fritz H., Clerin D., Fleury J.-P.: Org. Magn. Resonance 8, 269 (1976).
14. Witanowski M., Stefaniak L., Januszewski H. in the book: Nitrogen NMR (M. Witanowski, G. A. Webb, Eds), p. 166. Plenum Press, London 1973.
15. Westerman P. W., Botto R. E., Roberts J. D.: J. Org. Chem. 43, 2590 (1978).

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