^{13}C AND ^{15}N NMR SPECTRA OF OXIMES PREPARED BY NITROSATION OF ACTIVATED METHYLENE GROUP

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Dedicated to Professor Otto Exner on the occasion of his 65th birthday.

^{15}N and ^{13}C NMR spectra have been measured of the compounds type XC(=NOH)Y, where X, Y = COCH$_3$, CN, COOR, CONHR, and X + Y = C$_6$H$_4$(CO)$_2$. The (E)–(Z) isomerism at the C=NOH bond has been studied by means of ^{15}N labelling and stereospecific behaviour of the $^2J(^{15}$N, ^{13}C) coupling constants. The nitrosation of methyl cyanoacetate gives specifically the respective (E)-oxime, whereas that of acetoacetanilide gives the (Z)-isomer. The nitrosation of ethyl acetoacetate gives both (E)- and (Z)-oximes in a ratio of ca 1 : 10; the (E)-isomer is less stable and is transformed into the (Z)-isomer. The applicability of the $^1J(^{13}$C, ^{13}C) coupling constants and lanthanoid shift reagents to the study of (E)–(Z) isomerism of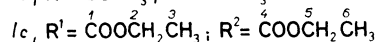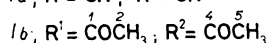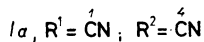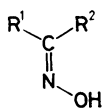 oximes with geminal carbonyl groups has also been verified. The ^{15}N NMR chemical shifts of the oximes studied correlate with their respective pK_a values measured in dimethyl sulfoxide according to the equation pK_a = $-0.11\delta^{15}$N + 13.44.

The isonitroso compounds derived from acetoacetic acid, cyanoacetic acid, acetyl-acetone, malonic acid derivatives, or 1,3-indanedione are applicable in analytical chemistry as precipitating agents for complexation of metals[1,2] or amino acids[3]. The nitrosation of activated methylene group in unsymmetrical compounds type X—CH$_2$—Y can give two isomeric, (E) and (Z), isonitroso compounds or oximes (see Scheme 1).

The isomerism of oximes was thoroughly studied earlier on the compound type R^1—CH(=NOH)—R^2 using various methods such as IR spectroscopy, dipole moment measurements, and very often also NMR spectroscopy[4−8]. On the other hand, the type of compounds dealt with in the present paper has not been subjected to any systematic study of (E)–(Z) isomerism except for the paper[9] dealing with the (E)–(Z) isomerism of 4-nitroso-1-phenyl-3-methylpyrazolin-5-one. The isomers of aldoximes and ketoximes were determined from ^{1}H and ^{13}C NMR spectra by using various measuring procedures, e.g. Karabastos and Taller[6] made use of the solvent effect on δ^1H, Levy and Nelson utilized the different relaxation of carbon atoms in ketoximes[5], in papers by Fraser[8] and Berlin[10] the lanthanide induced shift

(LIS) after addition of shift reagents is used to assignment of ketoximes. Soviet authors[11-13] utilized the different coupling constants $^1J(^{13}C, ^{13}C)$ of the bonds "*cis*" and "*trans*" with respect to the free electron pair of oxime nitrogen atom to differentiate between (E) and (Z) isomers of aldoximes and ketoximes.

Ia, $R^1 = \overset{1}{C}N$; $R^2 = \overset{4}{C}N$

Ib, $R^1 = \overset{1}{C}O\overset{2}{C}H_3$; $R^2 = \overset{4}{C}O\overset{5}{C}H_3$

Ic, $R^1 = \overset{1}{C}OO\overset{2}{C}H_2\overset{3}{C}H_3$; $R^2 = \overset{4}{C}OO\overset{5}{C}H_2\overset{6}{C}H_3$

Id, $R^1 = \overset{1}{C}ONH_2$; $R^2 = \overset{4}{C}ONH_2$

Ie, $R^1 = \overset{1}{C}H_3$; $R^2 = \overset{4}{C}H_3$

II

(E) (Z)

IIIa, $R^1 = \overset{1}{C}N$; $R^2 = \overset{4}{C}O\overset{5}{C}H_3$

IIIb, $R^1 = \overset{1}{C}O\overset{2}{C}H_3$; $R^2 = \overset{4}{C}OO\overset{5}{C}H_2\overset{6}{C}H_3$

IIIc, $R^1 = \overset{1}{C}O\overset{2}{C}H_3$; $R^2 = \overset{4}{C}ONHC_6H_5$
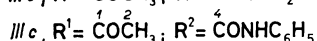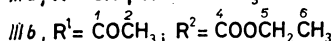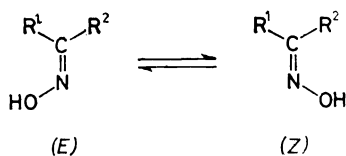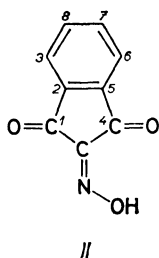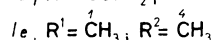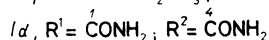
SCHEME 1

Other authors[14-17] for their studies chose a more complicated but univocal way of determination of oxime isomers by using isotopically labelled ^{15}N-oximes and

stereospecific interactions of the ^{15}N nucleus with protons and carbons in geminal or, in some cases, also more distant positions of the molecule.

The aim of the present paper was to characterize spectroscopically the oximes formed as isonitroso compounds in the nitrosation of activated methylene groups, to identify (in the case of unsymmetrical starting compounds) the (E) and (Z) isomers, and possibly to determine their ratio. For this purpose we have used the procedure similar to that of determination of isomeric azo coupling products at activated methylene groups[18−20] (i.e. the ^{15}N labelling and utilization of $^2J(^{15}N, ^{13}C)$). Moreover, we verified the methods using LIS and differences in $^1J(^{13}C, ^{13}C)$, 3-hydroxyimino-2,4-pentanedione (Ib) being chosen to represent this compound group.

EXPERIMENTAL

Compounds *Ia−Id, II, IIIa−IIIc* (Scheme 1) were prepared by nitrosation of the respective CH_2 groups with natrium nitrite in acid medium[21,22], compound *Ie* was obtained by reaction of acetone with hydroxylamine[21,22]. The ^{15}N isotopomers of these compounds were prepared by the same procedures using $Na^{15}NO_2$ (96% ^{15}N, Isocommerz Berlin). The ^2H isotopomer of compound *Ib* was obtained by repeated recrystallizations of compound *Ib* from heavy water.

The ^{15}N, ^{13}C, and ^1H NMR spectra were measured at 10·095, 25·047, and 99·602 MHz, respectively, using a JNM-FX 100 (Jeol) apparatus working in FT mode and equipped with a multinuclear tunable probe. The substances were measured as c. 20% solutions in hexadeuterio-dimethyl sulfoxide or deuteriochloroform at 300 K. The deuteriated solvents were used as the lock substances. The conditions of the measurements are given in ref.[18]. The ^1H and ^{13}C chemical shifts are related to the solvents signals: $CDCl_3$ ($\delta^{13}C = 77·00$, $\delta^1H = 7·25$), $(CD_3)_2SO$ ($\delta^{13}C = 39·60$, $\delta^1H = 2·55$). The ^{15}N chemical shifts are related to external nitromethane (25% ^{15}N, $\delta = 0·00$) in a coaxial capillary. Signals with negative values of chemical shift are shifted upfield. The chemical shifts were measured with an accuracy better than 0·012 ppm.

The dilution experiments and the measurements using the heteronuclear Overhauser effect were carried out with an AM 400 (Bruker) apparatus at 400·13 (^1H) or 100·61 (^{13}C) MHz. For the measurement of heteronuclear Overhauser effect we used the available[23] program of pulse sequence. For the presaturation of NH signal of 3-phenylhydrazono-2,4-pentanedione (IV) and of OH signal of compound *Ib* we used an interval of 5 s (denoted as D1 interval in the program).

The coupling constants $^1J(^{13}C, ^{13}C)$ were measured with an AM 300 (Bruker) apparatus at 75·54 MHz using the INADCOMP program[24], the sample being prepared by dissolving 0·8 g compound *Ib* in 1·5 ml $CDCl_3$ and addition of 40 mg relaxation agent (chromium(III) tris acetylacetonate). The pulse number 3 600 with the optimization at $^1J(^{13}C, ^{13}C) = 60$ Hz. The digital resolution 0·46 Hz/point.

The measurements of pK_a of the oximes type *I, II*, and *III* in dimethyl sulfoxide were carried out with an RTS-622 apparatus (Radiometer Copenhagen), the dimethyl sulfoxide was purified by a known procedure[25]. A freshly hydrated glass electrode and a calomel electrode with internal saturated solution of KCl in methanol were used for the measurements, 0·1M butylammonium hydroxide in methanol being used as the titrant. The system of electrodes was calibrated with 2,6-dinitrophenol and benzoic acid ($pK_a = 4·9$ and 11·0, respectively[26]). The detailed description of experimental conditions, way of calibration and evaluation are given in our previous papers[27,28]. Each measurement was repeated three times.

RESULTS AND DISCUSSION

Compounds *Ia−Id*, *II*, *IIIa−IIIc* were prepared by nitrosation in acid medium: the primary nitroso compounds are immediately isomerized into oximes.

Table I presents the values of ^{13}C NMR chemical shifts and $^nJ(^{15}N, ^{13}C)$ coupling constants, Table II gives the ^{15}N NMR chemical shifts. Compounds *Ia−Ie* and *II* exhibit only one set of ^{13}C NMR signals and a single ^{15}N NMR signal due to that they cannot form (E) and (Z) isomers at the C=N bond, being symmetrical. Although compounds *IIIa−IIIc* can form these isomers, compounds *IIIa* and *IIIc* also exhibit only one set of ^{13}C NMR signals and a single ^{15}N signal corresponding to the more stable isomer which does not change with temperature. Although it could be presumed that formation of an intramolecular hydrogen bond should stabilize the isomers (Z)-*IIIa* and (E)-*IIIc*, the opposite result follows from interpretation of the ^{13}C NMR spectra of ^{15}N isotopically labelled compounds *IIIa* and *IIIc*. The oxime (E)-*IIIa* forms the only isolable product of the nitrosation of methyl cyanoacetate, this oxim

TABLE I

^{13}C NMR chemical shifts (in ppm) of compounds *I*, *II*, *III* in hexadeuteriodimethyl sulfoxide and $^nJ(^{15}N, ^{13}C)$ coupling constants (in Hz)

Compound	Carbon						
	C-1	C-2	C-3	C-4	C-5	C-6	C=N
Ia	113·08	—	—	109·16	—	—	112·08
	(5·13)	—	—	(0·3)	—	—	(2·93)
Ib	195·68	25·91	—	201·00	30·94	—	115·13
	(11·35)	(0·3)	—	(1·22)	(0·3)	—	(0·97)
Ic[a]	[b]	[c]	114·48	[b]	[c]	114·48	114·19
Id[a]	[d]	—	—	[d]	—	—	149·06
Ie[a]	21·67	—	—	14·79	—	—	152·67
II[e]	185·68	140·40	[f]	180·12	140·81	[f]	146·13
	(9·00)	(2·44)	(0·3)	(0·5)	(0·3)	(0·3)	(1·95)
(E)-*IIIa*	109·10	—	—	159·29	53·64	—	125·95
	(1·71)	—	—	(9·82)	(0·85)	—	(2·56)
(Z)-*IIIb*	194·22	25·33	—	162·34	61·89	—	151·28
	(11·23)	(0·3)	—	(1·21)	(0·3)	(0·3)	(1·46)
(E)-*IIIb*[a]	198·78	30·30	—	160·99	63·94	14·03	150·23
(Z)-*IIIc*[g]	194·81	25·56	—	160·35	—	—	153·56
	(11·75)	(0·3)	—	(1·37)	—	—	(1·22)

[a] Measured in a sample with natural abundance of ^{15}N; [b] 161·81 or 160·68; [c] 62·51 or 62·63; [d] 163·57 or 163·33; [e] δ^{13} C-7 and δ^{13} C-8 = 136·13 or 136·54; [f] 123·32 or 123·79; [g] the carbon atoms of phenyl group: 138·41 (*i*-C), 119·34 (*o*-C), 129·17 (*m*-C), 124·14 (*p*-C).

being not isomerized with temperaure in contrast to the respective azo coupling product from benzenediazonium chloride where a mixture of (E)- and (Z)-isomers is formed but the (E)-isomer is transformed into the (Z)-isomer on standing of the reaction solution. A uniform product, (Z)-IIIc, was isolated from the nitrosation of acetoacetanilide, no further isomerization being observed. Similarly, the corresponding azo coupling reaction with benzenediazonium chloride produces the stable (Z)-isomer[20]. The nitrosation of acetoacetic acid gave a product exhibiting two sets of ^{13}C NMR signals and two ^{15}N NMR signals corresponding to the ratio (Z)-IIIb: (E)-IIIb = 10 : 1. The attempts at isolation of the isomer (E)-IIIb showed that it is unstable and is transformed into (Z)-IIIb. Also in azo coupling of benzenediazonium chloride with ethyl acetoacetate the (Z)-isomer is thermodynamically more stable[18]. The values of chemical shifts of compound (E)-IIIb were obtained by measuring the mixture with prevailing (Z)-IIIb isomer.

The ^{13}C NMR chemical shifts were assigned to the carbon signals on the basis of the magnitude of $^nJ(^{15}N, ^{13}C)$ coupling constants and their stereospecific behaviour, and with the use of proton-coupled spectra. Using the model compound Ib, we tried other methods of assignment of signals which were adopted earlier to the
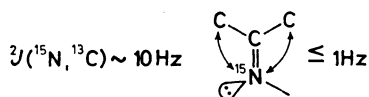
$$^2J(^{15}N, ^{13}C) \sim 10\,Hz \qquad \underset{\underset{N}{\overset{\|}{C}}}{\overset{C}{\underset{}{\diagdown}} \overset{}{\underset{}{C}} \overset{C}{\diagup}} \quad \leq 1\,Hz$$

TABLE II

^{15}N NMR chemical shifts (in ppm) and pK_a(DMSO) of compounds I, II, and III

Compound	$\delta^{15}N(N{=}OH)$	pK_a	S^a
Ia	$+69{\cdot}89$	$4{\cdot}39$	$0{\cdot}1$
IIb	$+17{\cdot}34$	$12{\cdot}11$	$0{\cdot}1$
Ic	$+19{\cdot}60$	—	—
Id^b	$-3{\cdot}99$	$12{\cdot}94$	$0{\cdot}03$
Ie	$-31{\cdot}80$	—	—
II	$+44{\cdot}50$	$8{\cdot}98$	$0{\cdot}01$
(E)-IIIa	$+63{\cdot}64$	$7{\cdot}31$	$0{\cdot}02$
(Z)-IIIb	$+21{\cdot}28$	—	—
(E)-IIIb	$+16{\cdot}81$	—	—
(Z)-$IIIc^{c,d}$	$+17{\cdot}53$	$11{\cdot}94$	$0{\cdot}04$

[a] The variance value of three measurements; [b] $\delta(NH_2) = -266{\cdot}28, -279{\cdot}58$; [c] $\delta(NH) = -242{\cdot}45$; [d] measured at 40°C.

analysis of spectra of oximes containing no geminal carbonyl or nitrile groups, and the results were compared with the method of ^{15}N isotope labelling.

Formula *V* gives, for the ^{15}N labelled isotopomer of *Ib*, the LIS values extrapolated to the addition of the shift reagent in the amount of 1 : 1 to the sample (the shift reagent concentration was 1 mol l^{-1}). The extrapolation was carried out from three additions of the shift reagent: 0·05, 0·1, and 0·2 mol l^{-1}. From the values given it follows that tris(2,2-bis(trideuteriomethyl)-1,1,1-trideuterio-6,6,7,7,8,8,8-heptafluoro--3,5-octanedionato)europium(III) (Eu(fod)$_3$-d$_{27}$) has a large effect on the carbonyl shifts in the oxime *Ib* and can be made use of for their assignment, whereas tris-(dipivalomethanato)europium(III) (Eu(dmp)$_3$), whose LIS values are given in parenthesis, cannot be utilized for the assignment of carbonyls because of the small LIS values and their low stereospecificity.
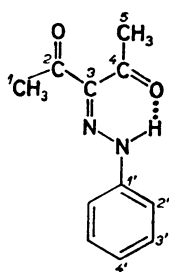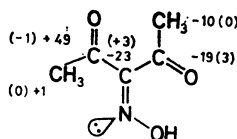

IV   *V*

Measurements of the $^1J(^{13}C, ^{13}C)$ coupling constant were used[11,12] to determine the isomerism at C=N bond of such oximes which have no geminal carbonyl groups. It was found that the $^1J(^{13}C, ^{13}C)$ coupling constant of the C=N carbon atom and the carbon atom "*cis*" to the free electron pair at oxime nitrogen is 8 to 10 Hz larger than that of the aldehyde or ketone, and the $^1J(^{13}C, ^{13}C)$ of the bond "*trans*" to this pair is c. 1 to 2 Hz smaller than that of the aldehyde or ketone. This fact is also true for the oximes with geminal carbonyl groups (see the $^1J(^{13}C, ^{13}C)$ value given in formula *VI* for compound *Ib* measured in deuteriochloroform). The ^{13}C NMR chemical shifts of methyl groups also were univocally assigned by application of the $^1J(^{13}C, ^{13}C)$ coupling constants in connection with the ^{15}N labelling.
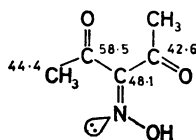
VI

Beside the (E) and (Z) isomerism at the C=N bond of oximes, these compounds also exhibit the possibility of *s-cis* and *s-trans* conformation of the OH proton and the therewith connected intra or intermolecular hydrogen bond. In order to study the proton orientation, we selected the compound *Ib* and two additional models: one with proved intramolecular hydrogen bond (3-phenylhydrazono-2,4-pentane-dione *(IV)*) and the other in which no intramolecular hydrogen bond is possible (propanoneoxime *(Ie)*). The existence of intramolecular hydrogen bond in compound *IV* in deuteriochloroform follows from the practically unchanged δ^1H .(=N—NH) value during the dilution experiments (Table III), another univocal proof consisting in the existence of the heteronuclear Overhauser effect of the NH proton and carbonyl connected therewith in the intramolecular hydrogen bond (see Fig. 1). The dilution experiments were carried out for both model compounds (*Ie* and

TABLE III

The concentration dependence of ^{1}H NMR chemical shift of the NOH proton in compounds *Ib* and *Ie* and of the =N—NH— proton in compound *IV*

Compound	Solvent	Concentration, mol l^{-1}	δ^1H, ppm
Ib	*a*	2	12·96^c
Ib	*a*	0·2	12·99
Ib	*a*	0·05	13·00
Ib	*a*	0·02	13·02
Ib	*a*	0·002	13·21
Ib	*b*	2	10·60
Ib	*b*	0·02	10·29
Ib	*b*	0·002	10·25
Ie	*a*	2	10·18
Ie	*a*	0·2	10·20
Ie	*a*	0·02	10·20
Ie	*b*	2	9·89
Ie	*b*	0·2	8·73
Ie	*b*	0·02	7·35
Ie	*b*	0·02	6·76
IV	*a*	0·5	14·12
IV	*a*	0·05	14·09
IV	*a*	0·005	14·07
IV	*b*	2	14·63
IV	*b*	0·2	14·72
IV	*b*	0·02	14·74
IV	*b*	0·002	14·73

^{a} (CD$_3$)$_2$SO; ^{b} CDCl$_3$; ^{c} $^2J(^{15}$N, OH$) = 1·34$ Hz in ^{15}N labelled compound.

IV) in two solvents. The values of chemical shifts are given in Table III. Compound IV forms the intramolecular hydrogen bond in deuteriochloroform and perhaps also in hexadeuteriodimethyl sulfoxide. The values of chemical shifts remain practically unchanged up to the dilution of 1 000 : 1. On the other hand, compound Ie represents the substances whose molecules associate in little solvating media (CDCl$_3$). On diluting the solution from 2M to 2 . 10^{-3}M we observed a decrease in the proton chemical shift δ(NOH) by 3·13 ppm. Although the upfield shift of the NOH proton signal of cmpound Ib in deuteriochloroform during a 100 fold dilution does not indicate any distinct association of the molecules, the intramolecular hydrogen bond was not proved by the measurement of heteronuclear Overhauser effect[23]. The measurement was carried out under the same conditions as that of the model IV. Neither could we prove the presence of two sets of ^{13}C signals when measuring the mixture of Ib and its NOD isotopomer in deuteriochloroform and in hexadeuteriodimethyl sulfoxide, which should exclude any strong hydrogen bond[29].

Although the conformation at C=N bond of compound Ib is stable toward both temperature and solvent (see Tables IV and V), the s-cis or s-trans conformation of the OH proton is not stable in the solution and, as far as the intramolecular hydrogen bond exists, is not strong enough to ensure conditions for the heteronuclear Overhauser effect of the NOH proton on the carbonyl bonded therein.

The ^{15}N NMR chemical shifts of the oximes type I (Scheme 1), where R^1 and R^2 are hydrogens, alkyl, or aryl groups were published[30] and vary from -2 to -65 ppm. The shift given[31] for compound Ie is $\delta(^{15}N) = -45\cdot9$ ppm in deuteriochloroform
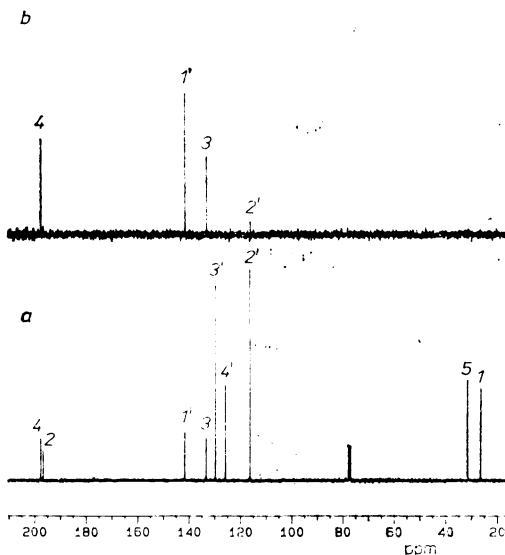

FIG. 1
^{13}C NMR spectrum (*a*) and heteronuclear difference NOE spectrum after selective irradiation of NH proton (*b*) of 3-phenyl-hydrazono-2,4-pentanedione (IV)

(the value measured by us is -45.2 ppm). The difference from the value $\delta(^{15}N) = -31.8$ ppm measured in hexadeuteriodimethyl sulfoxide is caused by different solvation of the acidic proton (see $\delta(^{1}H)$ of the NOH group). The ^{15}N NMR chemical shift of (E,E)-3,6-diacetyl-1,4,2,5-dioxadiazine[32], where there is an sp^2 carbon atom with electron–acceptor neighbours near the oxime nitrogen, is $+10.65$ ppm. This value supported our presumption that the values of ^{15}N NMR chemical shifts of the oximes having geminal carbonyl or nitrile groups would exhibit a down-field shift (i.e. would have values about zero or positive values of $\delta(^{15}N)$). The values of ^{15}N NMR shifts measured for the oximes prepared by us, of course, cover a relatively broad interval from -4 to $+70$ ppm. A possible explanation consists in the fact that the N–OH nitrogen atom is involved in a strongly conjugated system, and the electron density on it depends strongly on the type of the substituents R^1 and R^2. This is also confirmed by the fact that the dissociation constants of compounds I, II, and III measured in dimethyl sulfoxide are markedly different, hence a correlation

TABLE IV

Temperature dependence of ^{13}C NMR chemical shifts (in ppm) of compound Ib

Temperature, °C	Solvent	C-1	C-2	C-3	C-4	C-5
25	a	196·11	25·58	155·98	200·79	30·66
60	a	195·64	25·57	156·09	199·86	30·55
25	b	195·68	25·01	157·13	200·95	30·94
100	b	194·63	25·15	156·66	199·14	30·06
140	b	194·28	24·97	156·54	198·43	29·77

[a] $CDCl_3$; [b] $(CD_3)_2SO$.

TABLE V

Dependence of $^{n}J(^{15}N, ^{13}C)$ of compound Ib on solvent

Solvent	$^{n}J(^{15}N, ^{13}C)$, Hz		
	C-1	CN	C-4
$(CD_3)_2SO$	11·35	0·97	1·22
$(CD_3)_2CO$	11·48	a	a
$CDCl_3$	11·74	0·48	0·85

[a] Not observed in the spectrum at the digital resolution of 0·125 Hz/point.

can be made between δ^{15}N and pK_a of the oxime types *I*, *II*, and *III*. The resulting correlation equation reads as follows: $\mathrm{p}K_a = (-0.11 \pm 0.016)(\delta^{15}\mathrm{N}) + (13.44 \pm 0.69)$; $r = 0.962$, $n = 6$. The dissociation constant of compound *Ie* could not be determined due to very low acidity.

The difference between the ^{15}N chemical shifts of (E) and (Z) isomers of compound *IIIb* is 4·47 ppm. Similar differences within the limits from 0·2 to 5 ppm were published[30] for the (E) and (Z) isomers of oximes *I* in which R^1 and R^2 are alkyl groups.

The authors are indebted to Dr D. Uhrin for the measurements of connectivity of carbon atoms in compound Ib.

REFERENCES

1. Patil M. R., Haldar B. C.: J. Indian Chem. Soc. *50*, 569 (1973).
2. Talmar V. B., Haldar B. C.: J. Indian Chem. Soc. *49*, 785 (1972).
3. Eglite G., Oskaja V.: Latv. PSR Zinat. Akad. Vestis, Kim. Ser. *1972*, 605; Chem. Abstr. *78*, 52375 (1973).
4. Hawkes G. E., Herwig K., Roberts J. D.: J. Org. Chem. *39*, 1017 (1974).
5. Levy G. C., Nelson G. L.: J. Am. Chem. Soc. *94*, 4897 (1972).
6. Karabastos G. J., Taller R. A.: Tetrahedron *24*, 3347 (1968).
7. Fraser R. R., Bresse M.: Can. J. Chem. *61*, 576 (1982).
8. Fraser R. R., Capoor R., Bovenkaup J. W., Lacroix B. V., Pagotto J.: Can. J. Chem. *61*, 2616 (1984).
9. Ziegan D., Kleinpeter E., Wilde H., Mann G.: J. Prakt. Chem. *323*, 188 (1981).
10. Berlin K. D., Rengarajn S.: J. Org. Chem. *36*, 2912 (1971).
11. Krivdin L. B., Kalabin G. A., Nesterenko R. N., Trofimov B. A.: Zh. Org. Khim. *20*, 2477 (1984).
12. Krivdin L. B., Chuvashev J. A., Voronkov M. G.: Izv. Akad. Nauk SSSR, Ser. Khim. *1985*, 2137.
13. Krivdin L. B., Shcherbakov V. V., Kalabin G. A.: Zh. Org. Khim. *22*, 342 (1986).
14. Buchanan G. W., Dawson B. A.: Can. J. Chem. *55*, 1437 (1977).
15. Buchanan G. W., Dawson B. A.: Can. J. Chem. *56*, 2200 (1978).
16. Bremard C., Mouchel B., Sueur S.: J. Chem. Soc., Chem. Commun. *1982*, 300.
17. Allen M., Roberts J. D.: Can. J. Chem. *59*, 451 (1981).
18. Lyčka A.: Collect. Czech. Chem. Commun. *45*, 3354 (1980).
19. Lyčka A.: Collect. Czech. Chem. Commun. *49*, 2801 (1984).
20. Jirman J., Lyčka A.: Dyes Pigm. *8*, 55 (1987).
21. Touster O. in: *Organic Reactions* (R. Adams, Ed.), Vol. VII, Chap. 6. Wiley, New York 1953.
22. Sandler S. R., Karo W. in: *Organic Functional Group Preparation*, Vol. III, Chap. 11. Academic Press, New York 1972.
23. Sánchez-Ferrando F., Sanders J. K. M.: Magn. Reson. Chem. *24*, 539 (1987).
24. *Bruker Software Library*, Disr 85 (1985).
25. Kolthoff I. M., Reddy T. B.: Inorg. Chem. *1*, 189 (1962).
26. Kolthoff I. M., Chantooni M. K., Bhowmik S.: J. Am. Chem. Soc. *90*, 23 (1968).
27. Ludwig M., Pytela O., Kalfus K., Večeřa M.: Collect. Czech. Chem. Commun. *49*, 1182 (1984).

28. Ludwig M., Pytela O., Večeřa M.: Collect. Czech. Chem. Commun. *49*, 2593 (1984).
29. Hansen P. E.: Magn. Reson. Chem. *24*, 903 (1986).
30. Martin G. J., Martin M. L., Gouesnard J. P.: ^{15}N NMR Spectroscopy (P. Diehl, E. Fluck and R. Kosfeld, Eds). Springer, Berlin 1981.
31. Naulet N., Martin G. J.: Tetrahedron Lett. *1979*, 1493.
32. Fruttero R., Farrarotti B., Gasco A., Galestani G., Rizzoli C.: Liebigs Ann. Chem. *1988*, 1017.

Translated by J. Panchartek.