NMR STUDIES OF 1-PHENYLAZO-3-SUBSTITUTED-2-NAPHTHOLS IN SOLUTION AND IN THE SOLID STATE

Antonín LyČKA[a], Miroslav NeČAs[a], Josef Jirman[a], Jaroslav Straka[b] and Bohdan Schneider[b]

[a] *Research Institute of Organic Syntheses, 532 18 Pardubice-Rybitví and*
[b] *Institute of Macromolecular Chemistry,*
*Czechoslovak Academy of Sciences, 162 06 Prague*

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

The ^{1}H and ^{15}N NMR spectra of ^{15}N$_\alpha$-enriched 1-phenylazo-3-X-2-naphthols, where X = = COOH (*I*), X = COOCH$_3$ (*II*), and X = CONHC$_6$H$_5$ (*III*), have been measured in various solvents. The values of $^1J(^{15}$N$_\alpha$, H) and $\delta(^{15}$N) indicate that in CDCl$_3$, C$_6$D$_6$, CCl$_4$, and CD$_3$NO$_2$ solutions the compounds *I* and *III* exist practically completely in their hydrazone forms. The hydrazone form is stabilized by the hydrogen bond of COOH or CONH protons to the C(2)=O group. The compound *II* represents an equilibrium mixture of azo and hydrazone forms, since it cannot form a similar hydrogen bond. Moreover, the ^{15}N NMR spectra of compounds *I*—*III* have been measured in solid state by the CP/MAS technique. The results indicate the existence of two conformers differing by the conformation of COOCH$_3$ group in compound *II*, which is supported by the ^{13}C CP/MAS NMR spectrum of compound *II*.

The 1-phenylazo derivatives derived from 3-substituted-2-naphthols, particularly those having CONHC$_6$H$_5$ or substituted phenylaminocarbonyl group at the 3-position, are important organic pigments with broad technical applications[1]. As to real

I, X = OH
II, X = OCH$_3$
III, X = NH—⟨⟩
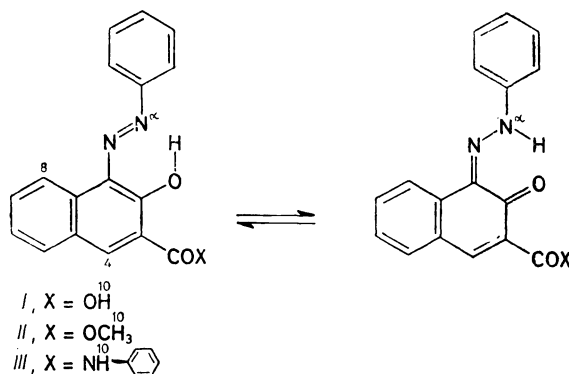
structure of these compounds in solution[2] and in solid state[3] their hydrazone form is usually preferred or is stated to coexist in a mixture with the azo form both in solution[4,5] and in solid state[6].

The aim of the present communication is to apply the NMR spectroscopy in solution and in the solid state to evaluate the azo–hydrazone tautomerism of the $^{15}N_{\alpha}$-enriched 1-phenylazo-3-substituted 2-naphthols *I—III*. The 1-phenylazo derivatives were selected, because they form solutions still applicable to the measurements of the ^1H and ^{15}N NMR spectra of $^{15}N_{\alpha}$-enriched compounds by long-term accumulation. If there are (particularly electron-acceptor) substituents in the phenyl groups, the compounds are quite insoluble in current solvents.

EXPERIMENTAL

The ^{15}N-enriched compounds *I* and *III* were obtained by azo coupling of the benzenediazonium chloride prepared from ^{15}N-aniline (96% ^{15}N) with 3-hydroxy-2-naphthoic acid or 2-hydroxy-naphthalene-3-carboxanilide[7]. Compound *II* was prepared by reaction of acid *I* chloride with methanol[8].

The ^1H NMR spectra were measured in the standard way at 99·602 MHz with a JNM-FX 100 (JEOL) apparatus in 10 mm NMR tubes. Due to low solubility, the samples for the measurement were saturated solutions in $CDCl_3$, C_6D_6, CCl_4, and CD_3NO_2. The temperature of the heating or cooling gas was measured with a thermocouple. The ^1H chemical shifts were related to internal tetramethylsilane ($\delta = 0·00$). The ^1H NMR spectra of the ten times diluted samples were measured at 400·13 MHz with a Bruker AM 400 apparatus. The ^{15}N NMR spectra of compounds *I—III* were obtained at 10·095 MHz with the JNM-FX 100 apparatus using the same samples as for the measurements of ^1H NMR spectra. The measurement conditions: spectral width 5 000 Hz, 8 K memory, pulse repetition 4 s, proton noise decoupling. The ^{15}N chemical shifts are related to external nitromethane (25% ^{15}N, $\delta = 0·0$).

The solid-state ^{15}N NMR spectra were measured at 20·28 MHz with a Bruker MSL 200 spectrometer using the CP/MAS technique[9,10] at room temperature. Alternation of the spin temperature in the rotating frame to suppress artifacts[11] and the flip-back pulse[12] were used. The samples were packed in double-bearing Al_2O_3 rotors supplied by Bruker. The magic angle was adjusted by minimization of the line width of the carbonyl carbon of glycine. Typical measurement conditions were as follows: 90° r.f. pulse: 5·5 µs, contact time 6 ms, pulse repetition time 5 s, number of transients 320, MAS frequency 5 kHz, spectral width 20 kHz, acquisition time 51 ms. The ^{15}N chemical shifts were referenced to solid NH_4Cl by sample replacement and re-calculated to nitromethane using $\delta(NH_4Cl) = -352·5$ (ref.[13]). The solid state ^{13}C CP/MAS NMR spectrum was taken on the same instrument at 50·32 MHz. The measurement conditions were as follows: 90° r.f. pulse: 5·5 µs, contact time 1 ms, pulse repetition time 5 s, number of transients 2 400, MAS frequency 4·5 kHz, spectral width 20 kHz, acquisition time 26 ms. The ^{13}C chemical shifts were referred to the carbonyl carbon atom of glycine ($\delta = 176·03$) by sample replacement. In all the cases positive values of chemical shifts denote downfield shifts.

RESULTS AND DISCUSSION

NMR spectroscopy represents a very appropriate method for investigation of azo––hydrazone tautomerism[14,15]. Several NMR characteristics have been proposed

for its evaluation[15]. The coupling constants $^1J(^{15}N_\alpha, H)_{exp}$ and chemical shifts $\delta(^{15}N)$ of the $^{15}N_\alpha$-enriched substances are applicable to solution of our problem of the measurements in solution because of the extremely low solubility of the substances measured. Table I presents the values of $^1J(^{15}N_\alpha, H)_{exp}$, the ^1H and $^{15}N_\alpha$ chemical shifts of compounds $I-III$ in various solvents and at various temperatures as well as the calculated contents of hydrazone forms in compounds II and III. The proton of $N_\alpha H$ group is split by the ^{15}N isotope (the spin number $I = 1/2$) into a doublet, the magnitude of the $^1J(^{15}N_\alpha, H)_{exp}$ coupling constant enabling the determination of azo and/or hydrazone forms content in the azo dyestuffs measured. The coupling constant $^1J(^{15}N_\alpha, H)_{exp}$ of compound I is independent of temperature and of the solvent used and corresponds to the compound existing in its hydrazone form. On the other hand, the magnitude of the coupling constants $^1J(^{15}N_\alpha, H)_{exp}$ of compound II depends on both the temperature and the solvent used, the coupling constants being distinctly smaller than those of compound I. Equation (1) was used to estimate the contents of the hydrazone form[16,17]:

$$\% \text{ hydrazone form } = 100 \left(^1J(^{15}N_\alpha, H)_{exp}/^1J(^{15}N_\alpha, H)_H\right), \qquad (1)$$

where $^1J(^{15}N_\alpha, H)_{exp}$ is the value measured for the respective tautomeric system and $^1J(^{15}N_\alpha, H)_H$ is that corresponding to the 100% content of hydrazone form. For the compounds without the second hydrogen bond (vide infra) it was suggested[17] to adopt the value $^1J(^{15}N_\alpha, H)_H = 96$ Hz. The content of hydrazone form in compound II varies from 60 to 78%, depending on the temperature and the solvent used. The coupling constants $^1J(^{15}N_\alpha, H)_{exp}$ in compound III are very similar to those in compound I, but they do show a certain dependence on temperature and solvent. Equation (1) was adopted also for the estimation of the hydrazone form content in compound III, but the coupling constant taken was $^1J(^{15}N_\alpha, H)_H = 92\cdot4$ Hz (see compound I), since the compounds able to form the second hydrogen bond (vide infra) have lower $^1J(^{15}N_\alpha, H)_H$ values[18] as compared with those unable to form this second hydrogen bond. The main difference between compounds I, III and the
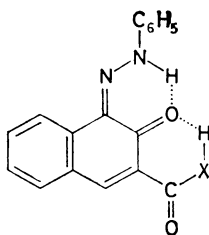
IV, X = O or NC_6H_5

TABLE I

Values of $^1J(^{15}N_\alpha, H)_{exp}$, ^1H, and ^{15}N chemical shifts of compounds $I-III$ in various solvents at various temperatures and calculated content of hydrazone form in compounds II and III

| Compound	Solvent	Temperature, K	$^1J(^{15}N_\alpha, H)_{exp}$ Hz ^{a}	$\%^b$	$\delta(^{15}N_\alpha)$	$\%^d$	$\delta(NNH)$	$\delta(H(4))^e$	$\delta(H(8))^e$	$\delta(H(10))$
I	$CDCl_3$	300	92·5	c	$-173·8$	c	16·56	8·88	8·45	13·70
I	$CDCl_3$	330	92·3	c	—	c	16·54	8·89	8·47	13·50
I	C_6D_6	300	92·5	c	$-178·0$	c	16·16	8·96	8·33	13·64
I	CD_3NO_2	300	92·3	c	—	—	16·33	8·76	8·57	13·45
II	$CDCl_3$	300	74·8	77·9	$-140·5$	76·5	16·89	8·41	8·46	3·96
II	$CDCl_3$	330	71·0	74·0	$-131·4$	73·1	16·74	8·33	8·41	3·86
II	C_6D_6	300	61·5	64·1	$-112·5$	66·3	16·85	8·28	8·56	3·76
II	C_6D_6	350	58·1	60·5	$-101·9$	62·3	16·50	8·27	8·56	3·79
II	CCl_4	300	58·2	60·6	—	—	16·57	8·28	8·50	3·91
III	$CDCl_3$	300	90·8	98·3	$-178·1$	c	16·81	8·96	8·37	11·57
III	$CDCl_3$	330	89·8	97·2	$-175·9$	c	16·79	8·96	8·43	11·46
III	C_6D_6	300	90·8	98·3	$-180·5$	c	16·46	9·08	8·25	11·57
III	C_6D_6	350	88·4	95·7	$-176·2$	c	16·50	9·06	8·28	11·45
III	CCl_4	300	90·5	97·9	—	—	16·86	8·94	8·43	11·25

^{a} ($\pm0·3$ Hz); ^{b} the percentage of hydrazone form calculated according to Eq. (1); ^{c} see the text; ^{d} the percentage of hydrazone form calculated according to ref.[19]; ^{e} the chemical shifts ^1H of the other aromatic protons are found within the interval of 7·10—8·00 ppm.

compound *II* consists in the fact that compounds *I* and *III* form the second intra-molecular[5,15] hydrogen bond (*IV*) which is very strong ($\delta(^1H)_{COOH}$ of compound *I* is 13·45 to 13·70), whereas compound *II* does not. This second intramolecular hydrogen bond represents a very significant stabilizing factor of the hydrazone form. The content of hydrazone form is practically 100% in compounds *I* and *III*, whereas that in compound *II* is roughly the same as in 1-phenylazo-2-naphthol (which exists as 70% 1,2-naphthoquinone 1-phenylhydrazone in deuteriochloroform[19]).

The ^1H chemical shifts of COOH and CONH protons in compounds *I* and *III* remain unaffected even after a tenfold dilution of the saturated solutions of the substances in deuteriochloroform, which was proved by measurements of ^1H NMR spectra at 400·13 MHz, and this fact can be considered — with respect to the very low concentrations used — to prove the intramolecular character of these hydrogen bonds.

At 99·602 MHz it is possible to assign — out of the aromatic protons — the ^1H chemical shifts of the H(4) protons (giving a singlet) and the H(8) protons at the peri position with regard to phenylhydrazone group. The other signals of aromatic protons form strongly overlapping multiplets within the region from 7·10 to 8·00 pm.

The ^{15}N chemical shifts in compounds *I* and *III* have the value of $-173\cdot8$ or are shifted even more upfield. The values are typical of almost 100% hydrazone compounds with two intramolecular hydrogen bonds. The value $\delta(^{15}N_\alpha) \approx -205$ of compound *V* is used as a standard value for a 100% hydrazone form with one intra-molecular hydrogen bond, whereas the value $\delta(^{15}N_\alpha) = -186\cdot3$ was measured[18] for the compound *VI* which also exists as 100% hydrazone form, however, stabilized
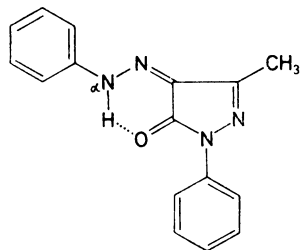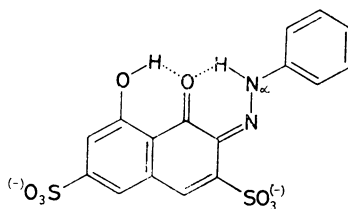
V   *VI*

by the second intramolecular hydrogen bond. The hydrazone form content in com-pound *II* was calculated with the use of $\delta(^{15}N_\alpha)$ values by the procedure given else-where[19]. Table I shows a reasonable agreement between the values of hydrazone form content determined in compound *II* by means of $^1J(^{15}N_\alpha, H)_{exp}$ and $\delta(^{15}N_\alpha)$.

For the compounds of the type *I*—*III*, which — if containing electron-acceptor substituents — are insoluble in current solvents, it is important that we might know the content of the hydrazone forms in solid phase. Earlier we described[20] the ap-

plication of ^{15}N CP/MAS NMR spectra to estimation of the hydrazone form content in solid state of model azo dyestuffs. The same technique has now been used to measure the solid compounds *I—III* at room temperature. The ^{15}N CP/MAS NMR spectra of the ^{15}N$_\alpha$-enriched compounds *I—III* are shown in Fig. 1. The compounds *I* and *III* exhibit one signal with the chemical shifts of $-190\cdot8$ and $-199\cdot9$, respectively. As compared with the values obtained in solution, the signals obtained by the measurement in solid state are shifted upfield by c. $10-17$ ppm. Similar differences were also found with the data of ref.[20] and were assigned to the differences in $\delta(^{15}N)$ of both the standard and the compounds in solution and solid state. Thus in solid state no distinct change was observed in the content of hydrazone form in compounds *I* and *III*, and these compounds exist also in solid state as 100% hydrazone forms. This result agrees with the X-ray diffraction data (see ref.[21] and the literature quoted therein) of similar substances which were proved to exist as planar structures in hydrazone forms with intramolecular hydrogen bonds. From the energy dispersive X-ray spectra[6] of compound *III* it was concluded that the solid substance exists as 52% hydrazone form and 48% azo form. This conclusion contradicts our results obtained from the ^{15}N CP/MAS NMR spectra. The difference of ^{15}N chemical shifts between the azo and hydrazone forms is c. 275 ppm for N$_\alpha$. If compound *III* had the composition given in ref.[6], then the signal of N$_\alpha$ would have to lie in the region about -30 ppm. Therefore we suppose that the method
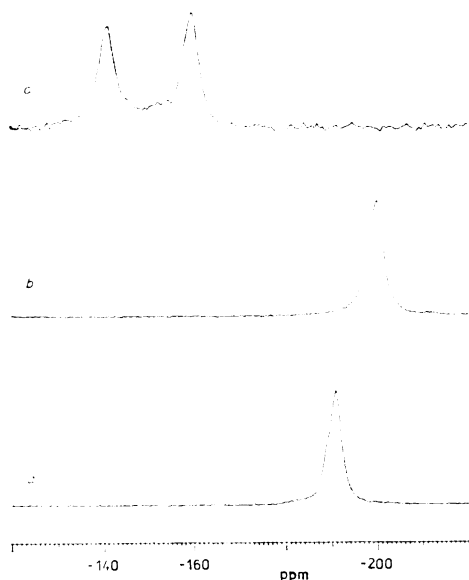

FIG. 1

The ^{15}N CP/MAS NMR spectra of compounds *I* (*a*), *II* (*c*), and *III*(*b*)

adopted[6] is inappropriate for characterization of the azo–hydrazone tautomerism. The method of energy dispersive X-ray spectra should be used to measure substances known to exist practically either as 100% azo or 100% hydrazone form, whereby the method would be verified.

The ^{15}N CP/MAS NMR spectrum of compound *II* (Fig. 1c) exhibits two signals with the chemical shifts of −141·2 and −159·8. Two ^{15}N chemical shifts were also observed in the ^{15}N CP/MAS NMR spectrum of 1-phenylazo-2-naphthol in solid state[20] where the difference between the ^{15}N chemical shifts varied (depending on the temperature) within the limits of 3·4−5·8 ppm and was ascribed to crystallographical nonequivalence in the unit cell. A difference of 3·4 ppm was described[3] for calcium(II) salt of (1-sulfo-4-methylphenylazo)-2-hydroxynaphthalene-3-carboxylic acid. In the case of compound *II*, however, the difference is markedly greater (18·6 ppm). The signals of ^{15}N CP/MAS NMR spectrum lying at −141·2 and −159·8 ppm can be interpreted as signals of two different azo–hydrazone forms in
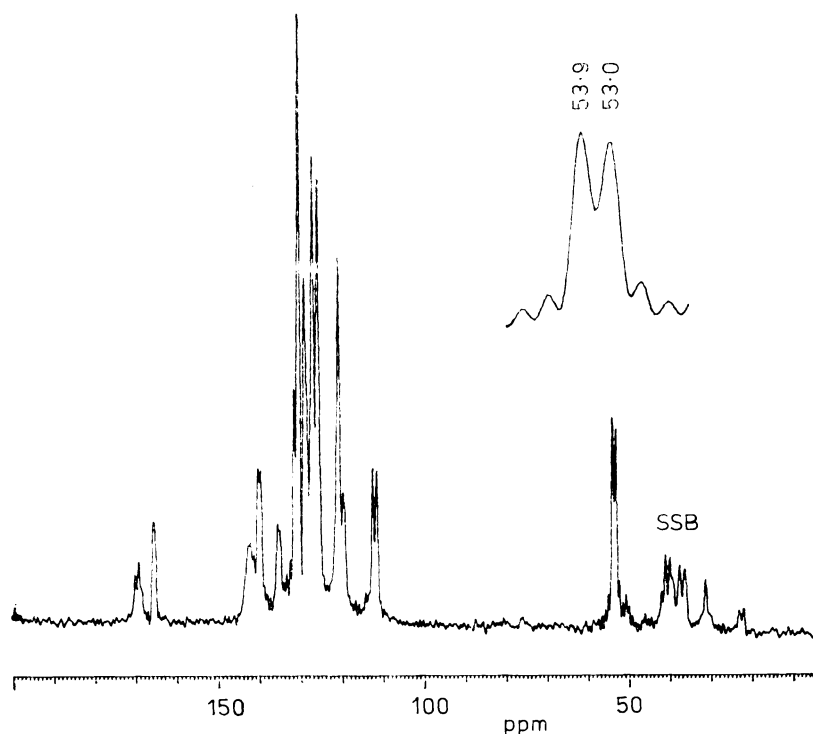

FIG. 2

The ^{13}C CP/MAS NMR spectrum of compound *II* (SSB denote spinning side-bands)

compound *II*, the proton exchange must be rapid judging from the signals half-widths. These two tautomerisms could arise either from the fact that compound *II* is composed of an amorphous and a crystalline parts or from a possibility of two conformations of compound *II* stable in solid state. In order to verify the existence of two stable conformers of compound *II*, we measured the ^{13}C CP/MAS NMR spectrum of this compound. The spectrum is given in Fig. 2, and it can be seen that it is composed of two sets of signals. The most striking splitting of signals is that of OCH_3 group. The bands of both the components are approximately of the same intensity, which is analogous to the two bands in the ^{15}N CP/MAS spectrum. All this agrees with the idea that there are two stable conformers present, formed by rotation around the C—$COOCH_3$ bond. As, according to the X-ray analysis, molecules of the type *II* are planar, our two conformers obviously are those given in formulas *VII* and *VIII* for the hydrazone form.
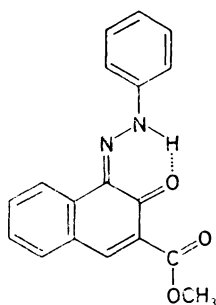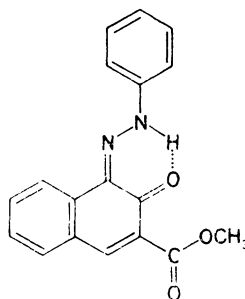
VII   *VIII*

Different situations with respect to interatomic distances (N—H, O—H) and electronic densities at the individual atoms then cause changes in the content of the tautomeric forms, the difference of 18·6 ppm for N_α atom corresponding to a 6·8% change in the azo or hydrazone form content (for a difference[20] of c. 275 ppm between "100%" azo and hydrazone compounds for N_α atom). The content of hydrazone forms determined from Eq. (*1*) and ref.[20] is c. 70 and 77% for the individual conformers of compound *II*. This content agrees well with the value of the hydrazone content determined in solution of compound *II* (Table I). Univocal evidence in support of the conformers *VII* and *VIII* could be provided by X-ray analysis.

REFERENCES

1. Herbst W., Hunger K.: *Industrielle Organische Pigmente*. Verlag Chemie, Weinheim 1987.
2. Gordon P. F., Gregory P. in: *Organic Chemistry in Colour*, p. 104. Akademie Verlag, Berlin 1983.

3. Harris R. K., Jonsen P., Packer K. J., Campbell C. D.: J. Chem. Soc., Perkin Trans. 2, *1987*, 1383.
4. Zaitsev B. E., Sycheva E. D., Sheban G. V., Lisitsina E. S., Michailova T. A., Rodionova Dyumaev K. M.: Zh. Org. Khim. *23*, 1743 (1987).
5. Mustroph H., Bartel R.: J. Prakt. Chem. *324*, 743 (1982).
6. Ivanova T. M., Sycheva E. D., Lisitsina E. S., Zaitsev B. E., Polyakova E. I., Dyumaev K. M.: Zh. Org. Khim. *23*, 372 (1987).
7. Lenoir J.: Peintures, Pigments, Vernis *36*, 700 (1960); Chem. Abstr. *63*, 5783e (1965).
8. Schmidt M., Moser E., Danuser J., Morry R., Müller W., Würgler J.: Ger. 921 223 (1954).
9. Andrew E. R.: Prog. Nucl. Magn. Reson. Spectrosc. *8*, 1 (1972).
10. Pines A., Gibby M. G., Waugh J. S.: J. Chem. Phys. *59*, 569 (1973).
11. Stejskal E. O., Schaefer J.: J. Magn. Reson. *18*, 560 (1975).
12. Tegenfeld J., Haeberlen U.: J. Magn. Reson. *36*, 453 (1979).
13. Witanowski M., Stefaniak L., Webb G. A.: Annu. Rep. NMR Spectrosc., B, *11* 144 (1981).
14. Fedorov L. A. in: *NMR Spectroscopy of Organic and Analytical Reagents and Their Complexes with Metal Ions*, Chap. 1. Nauka, Moscow 1987.
15. Mustroph H.: Z. Chem. *27*, 281 (1987).
16. Bekárek V., Dobáš J., Socha J., Vetešník P., Večeřa M.: Collect. Czech. Chem. Commun. *35*, 1046 (1970).
17. Lyčka A., Šnobl D.: Collect. Czech. Chem. Commun. *46*, 892 (1981).
18. Fedorov L. A., Lyčka A., Jirman J.: Izv. Akad. Nauk SSSR, Ser. Khim. *1989*, 2530.
19. Lyčka A., Šnobl D., Macháček V., Večeřa M.: Org. Magn. Reson. *16*, 17 (1981).
20. Lyčka A., Jirman J., Schneider B., Straka J.: Magn. Reson. Chem. *26*, 507 (1988).
21. Ball P., Nicholls C. H.: Dyes Pigments *3*, 18 (1982).

Translated by J. Panchartek.