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# $^{15}$N, $^{13}$C and $^{1}$H NMR spectra and azo-hydrazone tautomerism of some phenylazo compounds derived from 1,3- and 1,5-dihydroxynaphthalene

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Dedicated to Dr. A.T. Peters

## Abstract

Five phenylazo compounds derived from 1,3-dihydroxynaphthalene and 1,5-dihydroxynaphthalene and their $^{15}$N isotopomers were prepared by coupling with benzenediazonium salts. The products were as follows: 1-phenylazo-2,4-dihydroxynaphthalene **4**, 1,3-bis(phenylazo)-2,4-dihydroxynaphthalene **5**, 4-phenylazo-1,5-dihydroxynaphthalene **11**, X = H, 2-phenylazo-1,5-dihydroxynaphthalene **12**, X = H, and 4-(4-nitrophenylazo)-1,5-dihydroxynaphthalene **13**, X = NO$_2$. 1-Phenylazo-2,4-dihydroxynaphthalene **4** was also prepared by condensation of phenylhydrazine with Lawsone (**6**, 2-hydroxy-1,4-naphthoquinone). The $^{1}$H, $^{13}$C and $^{15}$N NMR spectra of these compounds were measured in hexadeuteriodimethyl sulfoxide. $^{1}$H and $^{13}$C chemical shifts were assigned using two-dimensional NMR spectroscopy. Azo-hydrazone tautomerism was studied using $^{13}$C and $^{15}$N chemical shifts. All of the compounds studied exist predominantly or completely in their hydrazone forms. © 2000 Elsevier Science Ltd. All rights reserved.

*Keywords:* Azo dyes; $^{1}$H, $^{13}$C and $^{15}$N NMR; Two-dimensional NMR; Azo-hydrazone tautomerism

## 1. Introduction

Relatively little attention has been paid to the benzenediazonium salt coupling products with 1,3-dihydroxynaphthalene and 1,5-dihydroxynaphthalene [1–5], for which several tautomers can theoretically exist which can be distinguished by NMR spectroscopy.

1,3-Dihydroxynaphthalene **1** (Scheme 1) can be considered either as a substituted 1-naphthol or a substituted 2-naphthol and, thus, two products **3** and **4** of benzenediazonium salt coupling reaction are possible. The subsequent coupling reaction of **3** and **4** should give same product **5**. The product of the condensation reaction of 2-hydroxy-1,4-naphthoquinone **6** (Lawsone) and phenylhydrazine **7** [6–8] was expected to be **4** rather than **8**, offering an alternative approach to **5** [9].

The preparation of 4-phenylazo-1,5-dihydroxynaphthalene **11** and 4-(4-nitrophenylazo)-1,5-dihydroxynaphthalene **13**, X = NO$_2$ (Scheme 2) by coupling reaction with 1,5-dihydroxynaphthalene has been described by Fischer and Bauer [10,11] Porai-Koshits et al. [12] have prepared **11** from

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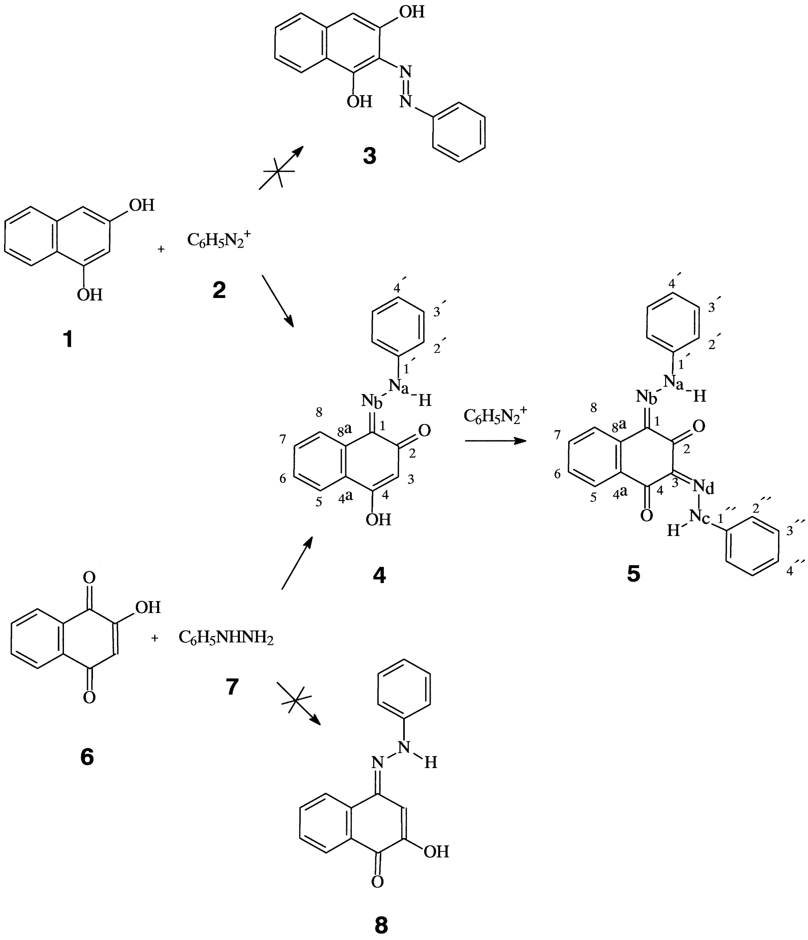


Scheme 1.

1-amino-5-hydroxy-naphthalene, followed by hydrolysis with aqueous sulphuric acid.

This work describes the measurement of $^1$H, $^{13}$C and $^{15}$N NMR spectra of the coupling products of diazonium salts with 1,3-dihydroxynaphthalene and 1,5-dihydroxynaphthalene in order to determine the structure of reaction products and to characterise the azo-hydrazone tautomeric equilibria.

## 2. Experimental

The compound **4** was prepared by standard coupling benzenediazonium chloride with 1,3-dihydroxynaphthalene [7] in alkaline medium. The condensation of Lawsone **6** with phenylhydrazine **7** was carried out according to published procedure [8] to give compound **4**. Compound **5** was prepared by standard coupling reaction of benzenediazonium chloride with compound **4** [9] and the $(^2H)_5$-isotopomer of **5** was obtained in the same way by coupling perdeuteriobenzenediazonium salt with compound **4**. Compounds **11** and **12**, prepared as a mixture by coupling benzenediazonium chloride with 1,5-dihydroxynaphthalene [10,11] in alkaline medium, were separated chromatographically. Compound **13** was prepared as described previously [10,11] and the crude product was crystallised from dimethylformamide to give pure **13**. $^{15}$N enriched compound were prepared as described above using $^{15}$N-aniline (20% $^{15}$N) and $Na^{15}NO_2$ (95%$^{15}$N).

The $^1H$ (360.13 MHz), $^{13}C$ (90.566 MHz) and $^{15}N$ (36.50 MHz) NMR spectra were recorded at 300 K on a Bruker AMX 360 spectrometer equipped with 5 mm broadband probe and 5 mm broadband inverse probe and a Silicon Graphic Indy computer. The compounds studied were measured in hexadeuteriodimethyl sulfoxide and $^1H$ and $^{13}C$ chemical shifts were referred to the central signal of the solvent [$\delta = 2.55$ ($^1H$) and 39.60 ($^{13}C$)]. The $^{15}N$ chemical shifts were referred to external nitromethane ($\delta = 0.0$) placed in a coaxial capillary. Positive values of chemical shifts denote downfield shifts with respect to standards.

Two dimensional H,H–COSY, NOESY, H,C–COSY, gs (gradient selected)-HMQC and gs-HMBC techniques were measured using standard microprograms provided by Bruker.

## 3. Results and discussion

### 3.1. $^1H$ and $^{13}C$ chemical shifts

The reaction of 1,3-dihydroxynaphthalene **1** with benzenediazonium ions **2** can give two reaction products: **3** and **4**. Lawsone **6** on reaction with phenylhydrazine **7** can give compounds **4** and **8**. Additional compounds are possible when tautomers **6** are taken into account. Our present work has shown that the same reaction product results from both reaction pathways and corresponds to **4**. The presence of additional compounds in the reaction mixture was negligible.

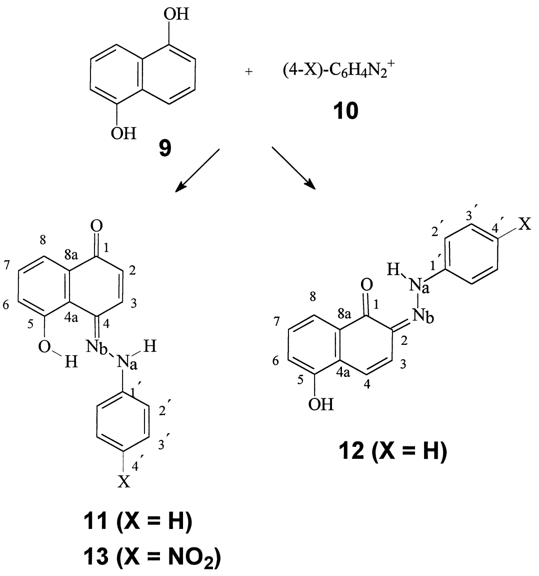
The $^1H$, $^{13}C$ and $^{15}N$ NMR spectra of **4** were measured and analysed. Two-dimensional NMR spectra [13] were used in order to assign proton and carbon chemical shifts unambiguously. H,H–COSY, NOESY, H,C–COSY, gs (gradient selected)-HMQC and gs-HMBC techniques [14] were applied. The $^1H$ and $^{13}C$ chemical shifts are collected in Table 1.

In the NOESY [15] spectrum of **3**, through-space proximity of isolated C(4)H proton with the *peri* proton H(5) from the non-substituted ring of naphthalene would have been expected. No such correlation is anticipated in **4** in line with its structure and none was observed. We found a long-range correlation between proton H-5 and

Table 1
$^1H$, $^{13}C$ and $^{15}N$ chemical shifts and $J(^{15}N_b, ^{13}C)$ coupling constants for **4** in $d_6$-DMSO

| H/C/N | $\delta(^1H)$ | $\delta(^{13}C)$ | Long-range interactions of proton(s) with appropriate carbon | $J(^{15}N_a, ^{13}C)$ |
|---|---|---|---|---|
| 1 | – | 124.27 | H(3), H(8) | 2.8 |
| 2 | – | 179.76 | | |
| 3 | 6.11 | 104.61 | | |
| 4 | 12.05 (OH) | 165.78 | H(5) | |
| 4a | – | 127.84 | H(3), H(8) | 4.2 |
| 5 | 7.98 | 123.54 | H(7) | |
| 6 | 7.51 | 126.42 | H(8) | |
| 7 | 7.64 | 130.26 | H(5) | |
| 8 | 8.41 | 121.76 | H(6) | 4.9 |
| 8a | – | 133.72 | H(5), H(7) | 9.1 |
| 1′ | – | 142.63 | H(3′) | 6.2 |
| 2′ | 7.67 | 116.07 | H(2′), H(4′) | 2.1 |
| 3′ | 7.51 | 129.79 | H(3′) | |
| 4′ | 7.22 | 124.88 | H(2′) | |
| $N_a$ | 16.18 (NH) | −197.9[abc] | | |
| $N_b$ | – | −20.1[a,b] | | |

[a] $\delta(^{15}N)$.
[b] $^1J(^{15}N, ^{15}N) = 11.1$ Hz.
[c] $^1J(^{15}N_a, ^1H) = 91.1$ Hz.



Scheme 2.

carbon C-4 (C–OH group resonating at 165.78 ppm) in gs-HMBC and no signal corresponding to the long-range correlation via $^{3}J(^{13}C, {}^{1}H)$ of C=O in gs-HMBC spectra was observed. From these facts it follows that C=O group must be in position 2 and not in 4.

Reaction of **4** with an additional mole of the diazonium salt gave **5**. Since the solubility of compound **5** is very low in $d_6$-DMSO, proton detected H,H–COSY, HMQC and HMBC techniques had to be used for assignment of $^{1}H$ and $^{13}C$ chemical shifts. In the $^{1}H$ NMR spectrum of **5**, there are two set of signals corresponding to two different phenyl groups. To differentiate between them, we prepared the $(^{2}H)_5$-isotopomer of **5** by coupling perdeuteriobenzenediazonium salt with compound **4**. The $^{1}H$ NMR spectra of **5** and $(^{2}H)_5$-**5** are shown in Fig. 1. Signals of protons H2″–H4″ are missing in the spectrum of $(^{2}H)_5$-**5**. Having compared HMQC spectra of **5** and $(^{2}H)_5$-**5**, $^{13}C$ chemical shifts of two phenyl groups could be assigned unambiguously.

The $^{1}H$ and $^{13}C$ chemical shifts in compound **5** are collected in Table 2.

The reaction of 1,5-dihydroxynaphthalene **9** reacting with benzenediazonium ions **10** gave two reaction products **11** and **12** that were separated chromatographically. The minor component **12** gave NMR spectra of standard quality and both $^{1}H$ and $^{13}C$ chemical shifts were assigned (Table 3) in a similar way to that for compound **4** as described above.

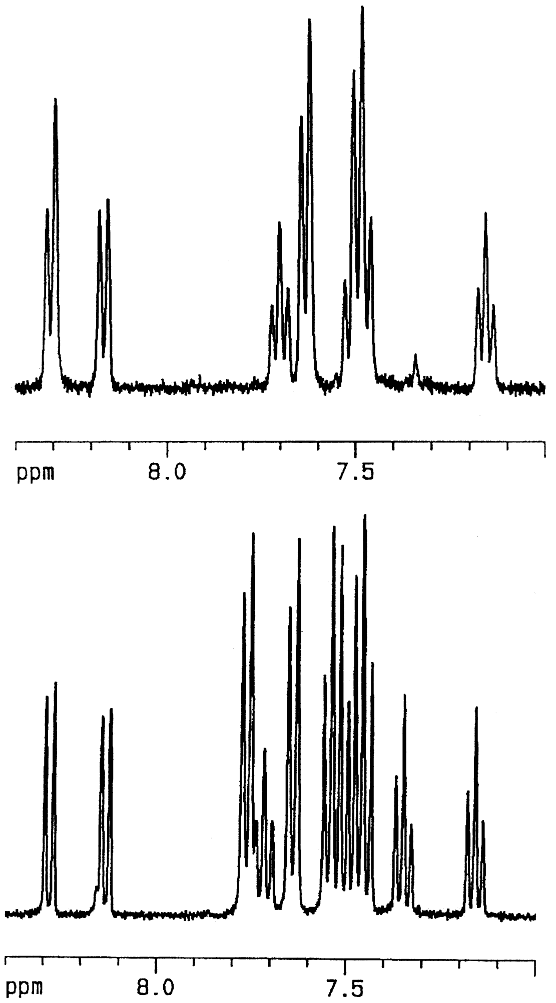


Fig. 1. $^{1}H$ NMR spectrum of **5** in $d_6$-DMSO (lower trace) and $^{1}H$ NMR spectrum of $(^{2}H)_5$-**5** in $d_6$-DMSO (upper trace).

Table 2
$^{1}H$, $^{13}C$ and $^{15}N$ chemical shifts for **5** in $d_6$-DMSO

| H/C/N | $\delta(^{1}H)$ | $\delta(^{13}C)$ | Long-range interactions of proton(s) with appropriate carbon |
|---|---|---|---|
| 1 | – | 177.04 | |
| 2 | – | 127.27 | |
| 3 | – | 179.71 | |
| 4 | – | 128.39 | |
| 4a | – | 131.14 | |
| 5 | 8.31 | 122.25 | H(6) |
| 6 | 7.77 | 133.65 | H(5) |
| 7 | 7.53 | 126.57 | H(8) |
| 8 | 8.17 | 126.57 | H(7) |
| 8a | – | 135.88 | H(8) |
| 1′ | – | 142.22 | H(3′) |
| 2′ | 7.69 | 115.55 | H(2′), H(4′) |
| 3′ | 7.51 | 129.63 | H(3′) |
| 4′ | 7.21 | 124.29 | H(2′) |
| 14″ | – | 142.34 | H(3″) |
| 24″ | 7.89 | 117.71 | H(2″), H(4″) |
| 34″ | 7.59 | 129.49 | H(3″) |
| 44″ | 7.39 | 127.17 | H(2″) |
| $N_a$ | 15.69 (NH) | −208.6[a] | |
| $N_b$ | – | −27.4[a] | |
| $N_c$ | 15.14(NH) | −182.9[a] | |
| $N_d$ | – | 8.2[a] | |

[a] $\delta(^{15}N)$.

The $^1$H NMR spectrum of compound **11**, which is the major reaction product, is shown in Fig. 2.

Proton NMR signals of phenyl group are broadened and the pattern did not change when the spectrum was recorded at elevated temperature. We were unable to obtain meaningful data from the $^{13}$C NMR spectrum because very broad overlapping signals were observed. The abovementioned effect can be ascribed to a moderately fast exchange on the NMR time scale. The $^1$H chemical shifts are collected in Table 4.

Table 3
$^1$H, $^{13}$C and $^{15}$N chemical shifts and $J(^{15}N_b, ^{13}C)$ coupling constants for **12** in $d_6$-DMSO

| H/C/N | $\delta(^1H)$ | $\delta(^{13}C)$ | Long-range interactions of proton(s) with appropriate carbon | $J(^{15}N_a, ^{13}C)$ |
|---|---|---|---|---|
| 1 | – | 168.91 | H(3), H(8) | |
| 2 | – | 130.06 | H(4) | |
| 3 | 7.29 | 123.77 | | 7.6 |
| 4 | 7.47 | 115.07 | | 4.2 |
| 4a | – | 125.81 | H(3), H(8) | |
| 5 | – | 153.58 | H(4), H(6), H(7) | |
| 6 | 7.15 | 116.01 | H(8) | |
| 7 | 7.33 | 126.73 | H(5) | |
| 8 | 7.83 | 116.45 | H(6) | |
| 8a | – | 132.58 | H(4) | |
| 1′ | – | 144.97 | H(3′) | 5.9 |
| 2′ | 7.79 | 118.58 | H(2′), H(4′) | 2.8 |
| 3′ | 7.52 | 129.47 | H(3′) | |
| 4′ | 7.35 | 127.49 | H(2′) | |
| $N_a$ | – | 42.9[a] | | |

[a] $\delta(^{15}N)$.

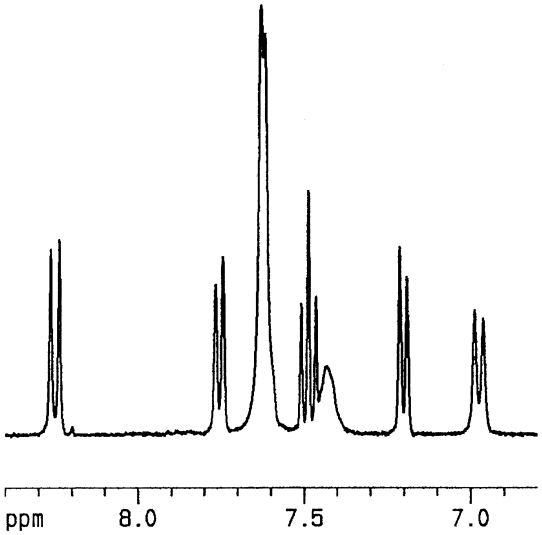


Fig. 2. $^1$H NMR spectrum of **11** in $d_6$-DMSO.

We decided to prepare the 4-nitro analogue **13** of **11**. Probably due to a shift in azo-hydrazone equilibrium (vide infra), and unlike compound **11**, **13** gave NMR spectra of reasonable quality and all $^1$H and $^{13}$C chemical shifts could be assigned.

### 3.2. $^{15}N$ chemical shifts

Since the solubility of compounds studied was very low in most cases it was necessary to prepare $^{15}$N enriched compounds for the measurement of $^{15}$N chemical shifts. Differential degrees of $^{15}$N enrichment (usually 20% $^{15}N_a$, 95% $^{15}N_b$) enabled the unambiguous assignment of the $^{15}$N chemical shifts undoubtedly. Moreover, it was possible to determine $^nJ(^{15}N_b, ^{13}C)$ by measuring $^{13}$C NMR spectra of $^{15}$N enriched dyes and to use these values for independent control of $^{13}$C chemical shift assignment because of the stereospecific behaviour of some $^nJ(^{15}N, ^{13}C)$ coupling constants [16]. The values of $\delta(^{15}N)$ and $^nJ(^{15}N_b, ^{13}C)$ coupling constants are given in Tables 1–3 and 5.

### 3.3. Azo-hydrazone tautomerism

The application of NMR methods for determination of azo-hydrazone tautomeric equilibria has been reviewed [17,18].

Table 4
$^1$H chemical shifts for **11** in $d_6$-DMSO

| H | $\delta(^1H)$[a] |
|---|---|
| 2 | 6.97 |
| 3 | 8.25 |
| 6 | 7.20 |
| 7 | 7.48 |
| 8 | 7.75 |
| 2′ | 7.62[b] |
| 3′ | 7.62[b] |
| 4′ | 7.43[b] |

[a] $\delta(OH) = 12.01$.

[b] Broadened signal.

Table 5
$^{1}$H, $^{13}$C and $^{15}$N chemical shifts and $J(^{15}N_b, ^{13}C)$ coupling constants for **13** in $d_6$-DMSO

| H/C/N | $\delta(^{1}H)$ | $\delta(^{13}C)$ | Long-range interactions of proton(s) with appropriate carbon |
|---|---|---|---|
| 1 | – | 183.21 | H(3), H(8) |
| 2 | 6.83 | 129.89 | |
| 3 | 8.25 | 126.99 | |
| 4 | – | 139.51 | |
| 4a | – | 117.03 | H(3), H(8) |
| 5 | –[a] | 156.17 | H(7) |
| 6 | 7.27 | 120.98 | H(8) |
| 7 | 7.49 | 129.89 | H(5) |
| 8 | 7.62 | 117.61 | H(6) |
| 8a | – | 13059 | |
| 1′ | – | 148.40 | H(3′) |
| 2′ | 7.36 | 113.74 | H(2′), H(4′) |
| 3′ | 8.30 | 126.15 | H(3′) |
| 4′ | –[b] | 141.44 | H(2′) |
| $N_a$ | –[c] | −223.4[d] | |
| $N_b$ | – | −76.0[d] | |

[a] $\delta(O\boldsymbol{H}) = 11.92$.

[b] $\delta(^{15}N)(NO_2) = -11.9$.

[c] $\delta(N\boldsymbol{H}) = 12.39$.

[d] $\delta(^{15}N)$.

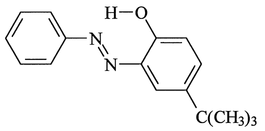
Based on $\delta(^{13}C)$ of $C(2)=O$ group = 179.76 we can conclude that **4** exists almost completely in a hydrazone form. The hydrazone content calculated from $^{15}$N chemical shifts [19] using $N_a$ is 97,3% and $N_b$ is "101.9"%. The calculated hydrazone content for $N_b$ is formally higher than 100% as a result of the choice of standards used for the calculation [19]. Choice of standard is particularly fundamental with tautomeric mixtures approaching either practically pure hydrazone form, as in **4**, or pure azo compounds.

The electron withdrawing substituents on phenyl ring originating from diazonium salt increase the hydrazone form content in suitable azo-hydrazone tautomeric systems. For example, the hydrazone content in benzenediazonium salt coupling product with 2-naphthol [19] is ca. 70% while in 4-nitrobenzenediazonium salt coupling product with the same passive component [20] is nearly 100%. In compound **4**, electrondonating hydroxy group in the passive component in position **4** has nearly the same effect.

The assignment of $^{15}$N chemical shifts in **5** is based on the measurement of selectively enriched compounds and is, thus, unambiguous. The hydrazone form strongly predominates in both tautomeric systems of compound **5**.

The hydrazone content in **12** calculated from $\delta(^{15}N_a) = 58.3\%$ which is slightly lower value than that in 1-hydroxy-2-phenylazonaphthalene (ca 78% at 300 K) in deuteriochloroform [21].

Compound **13** exists practically completely in its hydrazone form (Scheme 2) as inferred from $\delta(^{13}C)$ of $C(1)=O$ group = 183.21 which is close to the $^{13}$C chemical shift of the carbonyl group in 1,4-naphthoquinone [22] ($\delta(^{13}C) = 184.7$). An interesting structural feature of **13** is the existence of a strong hydrogen bond between the 5-hydroxy group proton in position 5 and nitrogen $N_b$. The consequence of this hydrogen bonding is that $^{15}N_b$ now resonates at considerably lower frequency ($\delta(^{15}N_b) = -76$) which represents a *ca* 60 ppm upfield shift with respect to $\delta(^{15}N_b)$ in compounds existing completely in a hydrazone form without such second hydrogen bonding, e.g. in 3-methyl-1-phenylpyrazole-4,5-dione 4-phenylhydrazone [18]. Very similar difference in $^{15}$N chemical shifts (57.3 ppm) resulting from hydrogen bonding was observed in **14** [19], in which the $^{15}$N chemical shift of the hydrogen bonded nitrogen is δ 69.4 while that of the non-H-bonded $^{15}$N atom is δ 126.9 ppm.



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