

## IR SPECTRA AND STRUCTURE OF 3-INDAZOLINONES AND THEIR DERIVATIVES

J.KLICNAR, B.OLBRACHTOVÁ - NYKLOVÁ, J.ŠLOSAR, P.ŠLOSAR and M.VEČEŘA

*Organic Chemistry Department,  
Institute of Chemical Technology, 532 10 Pardubice*

Received March 18th, 1976

Constitution of 3-indazolinone, its 5-nitro-, 6-nitro-, and 6-amino-derivatives has been studied with the use of IR spectroscopy and isotopic substitution of hydrogen and nitrogen. Bands of characteristic vibration of some functional groups of the both tautomers have been assigned. Constitution is given of acetylation products of 3-indazolinones and methylation products of 6-nitro-3-indazolinone. With three 1-substituted 3-indazolinones the effect of solvent on the ratio of the both tautomers has been determined. Quinoid structure of the dyestuff prepared from 3-indazolinone and N,N-diethyl-1,4-diaminobenzene has been proved spectroscopically.

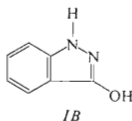
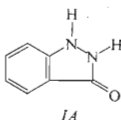
3-Indazolinone (*I*) is used as colour coupler in multi-layer colour photography; it gives a purple dyestuff on action of the developer — N,N-diethyl-1,4-diaminobenzene in alkaline medium in the presence of silver chloride. IR spectrum of the dyestuff has not yet been studied. Lactam structure *IA* was suggested by O'Sullivan<sup>1</sup> for the compound *I* in solid state, Janssen<sup>2</sup> suggested the predominance of *IB* form, Evans and coworkers<sup>3</sup> give *IB* as the most probable structure, although this compound shows absorption in the region 1600–1642 cm<sup>-1</sup> (see ref.<sup>3</sup>). The aim of the present paper is to interpret the IR spectra of the tautomeric substance *I*, its derivatives, and the abovementioned dyestuff.

In contrast to the authors mentioned we could find two bands in the carbonyl spectral region of the compound *I*: at 1640 and at 1624 cm<sup>-1</sup> (KBr disc), the both values being lower by 10 cm<sup>-1</sup> when measured in Nujol (Table I). The wave number of the first band corresponds to the carbonyl of the tautomeric form *IA*. For the sake of assignment of the second band we also measured the spectrum of [2-<sup>15</sup>N]-3-indazolinone and found a shift -11 cm<sup>-1</sup>.

The absorption band at 1624 cm<sup>-1</sup> could be assigned either to valence vibration of C=N group of the lactim form *IB* or to vibration  $\delta(\text{N—H})$  of the tautomer *IA*. With respect to that with *cis*-amides the vibration  $\delta(\text{N—H})$  is IR-inactive due to central symmetry of the dimer<sup>4</sup>, the band at 1624 cm<sup>-1</sup> can be assigned to vibration  $\nu(\text{C=N})$ . A similar value 1622 cm<sup>-1</sup> was found for 1*H*-indazole<sup>1</sup>. On the contrary, Janssen<sup>2</sup> presumed the band  $\nu(\text{C=N})$  at 1560 cm<sup>-1</sup> for the compound *I* and its derivatives. Our assignment is supported also by the fact that the shape of spectrum

in the region  $1500-1700\text{ cm}^{-1}$  does not change on deuteration of the compound *I*. The value  $-11\text{ cm}^{-1}$  also corresponds to the difference of wave numbers of the bands  $\Delta\nu(\text{C}=\text{N})$  for the  $^{14}\text{N}$  and  $^{15}\text{N}$  derivatives of the type of Schiff's bases<sup>5</sup>. In the spectrum of 6-nitro-3-indazolinone (*II*) the band with the highest wave number is of medium intensity, having two maxima ( $1643, 1660\text{ cm}^{-1}$ ). The lower intensity of the band  $\nu(\text{C}=\text{O})$  was found also with 5-nitro-3-indazolinone (*III*); in spectrum of 6-amino-3-indazolinone (*IV*) three very intensive bands at  $1622, 1615,$  and  $1590\text{ cm}^{-1}$  can be observed which were (with respect to the structure of the compound *IV*) assigned to  $\nu(\text{C}=\text{O}), \delta(\text{N}-\text{H}),$  and  $\nu(\text{C}=\text{N}),$  respectively.

Shifts to lower wave numbers in spectrum of the compound  $[^{15}\text{N}]\text{-I}$  were also found with the bands at  $1412\text{ m} (-6), 1225\text{ s} (-6), 1170\text{ s} (-11), 676\text{ m} (-7), 597\text{ m} (-7),$  and  $544\text{ m} (-6)\text{ cm}^{-1}$ . In spite of a certain extent of coupling between the vibrations it can be presumed that the changes will occur predominantly with the vibration frequencies of nitrogen bonds in 2-position of the tautomers *IA* and *IB*,



*i.e.*  $=\text{C}-\text{N}, \text{N}-\text{N}, \text{N}=\text{N}$  and  $\text{N}-\text{H}$ . The bands  $\nu(\text{N}-\text{N})$  and  $\delta(\text{N}-\text{N})$  of triazenes were identified by Lüttke<sup>6</sup> at  $1202$  and  $637\text{ cm}^{-1}$ , respectively. For azo com-

TABLE I  
Band Frequencies (in  $\text{cm}^{-1}$ ) in Spectra of 3-Indazolinones *I-IV*

| Sample <sup>a</sup>          | $\nu(\text{C}=\text{O})$          | $\nu(\text{C}=\text{N})$ | $\delta(\text{CONH})$<br>$\delta(\text{COND})$ | $\nu(\text{N}=\text{N})$ | $\delta(\text{N}-\text{H})$<br>$\delta(\text{N}-\text{D})$ | $\omega(\text{O}-\text{H})$<br>$\omega(\text{O}-\text{D})$ |
|------------------------------|-----------------------------------|--------------------------|--|--------------------------|--|--|
| <i>I</i>                     | 1 640 vs                          | 1 624 s                  | 1 495 s  | 1 225 s                  | 1 170 vs   | 814 m, b   |
| $[2-^{15}\text{N}]\text{-I}$ | 1 640 vs                          | 1 613 s                  | 1 495 s  | 1 219 s                  | 1 159 vs   | 814 m, b   |
| $[^2\text{H}_2]\text{-I}^b$  | 1 650 vs                          | 1 634 s                  | 1 132 s  | 1 225 s                  | 860 vs   | 594 m, b   |
| <i>II</i>                    | 1 643 s<br>1 660 m                | 1 623 m                  | 1 490 m, sh                                    | 1 227 s                  | 1 168 s  | 818 w  |
| <i>III</i>                   | 1 635 sh, m                       | 1 614 vs                 | 1 490 s  | —                        | 1 158 s  | 817 w  |
| <i>IV</i>                    | 1 622 vs<br>1 615 vs <sup>c</sup> | 1 590 vs                 | 1 492 s  | 1 205 s                  | 1 160 m  | 825 m  |

<sup>a</sup> vs very strong, s strong, m medium, w weak, b broad band, sh shoulder; <sup>b</sup> in Nujol; <sup>c</sup> band  $\delta(\text{N}-\text{H})$ .

pounds and Schiff's bases a sharp band  $\nu(\text{C}_6\text{H}_5\text{—N=})$   $1145\text{ cm}^{-1}$  is characteristic<sup>7</sup>. Mashima<sup>8</sup> gives the value  $\nu(\text{N—N})$   $1130\text{ cm}^{-1}$  for hydrazides of carboxylic acids. We suppose that the mentioned band at  $1225\text{ cm}^{-1}$  belongs to valence vibration of N—N= group of the tautomer *IB*.

Spectrum of the compound *I* (KBr disc) contains a broad band at  $2600\text{—}3150\text{ cm}^{-1}$  belonging to the associated groups O—H and N—H, because the both forms *IA* and *IB* are associated as dimers in solid state, which is similar to 1-substituted 3-indazolinones<sup>2</sup>. In spectrum of the compound [<sup>2</sup>H<sub>2</sub>]-*I* having the deuterium atoms in heterocyclic ring the O—D and N—D groups absorb by a broad band with two maxima at  $2105$  and  $2295\text{ cm}^{-1}$ . In the region of deformation vibrations of O—H and N—H groups new bands are observed at  $1132$ ,  $1049$ ,  $860$ ,  $679$ ,  $594$ , and  $475\text{ cm}^{-1}$  instead of the medium intensive bands of the compound *I* at  $1495$ ,  $1348$ ,  $1170$ ,  $889$ ,  $814$ , and  $660\text{ cm}^{-1}$ .

The absorption band at  $1495\text{ cm}^{-1}$  probably belongs to vibration of the group CO—NH (amide II), see ref.<sup>8</sup>, the band of the CO—ND group being at  $1132\text{ cm}^{-1}$  (the deuteration factor 1.3). The band at  $1170\text{ cm}^{-1}$  could be assigned (with respect to the mentioned shift  $-11\text{ cm}^{-1}$  accompanying the change from  $2\text{-}^{14}\text{N}$  to  $2\text{-}^{15}\text{N}$ ) to the deformation vibration of the N—H group in 2-position of the tautomer *IA* which is coupled with carbonyl (amide II) and possibly also with NH group in 1-position. The deuterated species has an absorption band at  $860\text{ cm}^{-1}$  (deuteration

TABLE II  
Bands of Characteristical Frequences in Spectra of Methyl- and Acetyl Derivatives of 1*H*-Indazole

| Sample <sup>a</sup> | $\nu(\text{C=O})$    |           |            | $\nu(\text{NO}_2)$ |             | $\nu(\text{C—O})$ |
|---------------------|----------------------|-----------|------------|--------------------|-------------|-------------------|
|                     | 3-oxo-               | 1-acetyl- | 3-acetoxy- | <i>sym</i>         | <i>asym</i> |                   |
| <i>Ila</i>          | 1 660 vs             | —         | —          | 1 352 vs           | 1 530 s     | —                 |
| <i>Iib</i>          | —                    | —         | —          | 1 351 vs           | 1 528 s     | 1 242 s           |
| <i>Iic</i>          | —                    | —         | —          | 1 351 vs           | 1 537 vs    | 1 230 s           |
| <i>V</i>            | —                    | 1 720 vs  | 1 772 vs   | —                  | —           | 1 200 vs          |
| <i>VI</i>           | —                    | 1 735 vs  | 1 760 vs   | 1 350 vs           | 1 531 vs    | 1 202 vs          |
| <i>VII</i>          | —                    | 1 716 vs  | 1 779 vs   | 1 344 vs           | 1 523 s     | 1 168 vs          |
| <i>VIII</i>         | 1 671 s <sup>b</sup> | 1 715 vs  | 1 786 vs   | —                  | —           | 1 200 vs          |
| <i>IX</i>           | 1 650 m              | 1 686 vs  | —          | —                  | —           | —                 |
| <i>X</i>            | 1 665 s              | 1 695 vs  | —          | 1 330 vs           | 1 522 s     | —                 |
| <i>XI</i>           | 1 665 s              | 1 704 vs  | —          | 1 323 vs           | 1 515 vs    | —                 |
| <i>XII</i>          | 1 625 m              | 1 694 vs  | —          | —                  | —           | —                 |
|                     | 1 665 s <sup>b</sup> |           |            |                    |             |                   |

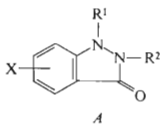
<sup>a</sup> In KBr discs; for intensities see footnote <sup>a</sup> in Table I; <sup>b</sup> carbonyl of 6-acetylamino group.

factor 1.36). The broad band of medium intensity at  $814\text{ cm}^{-1}$  belongs to deformation vibration of the OH group of lactime form *IB*,  $\omega(\text{O}-\text{D})\ 594\text{ cm}^{-1}$  (deuteration factor 1.37).

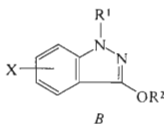
In the case of the 6-nitro derivative *II* we tried to characterize the both tautomers by alkylation with diazomethane. The reaction product was separated chromatographically to give the more polar compound *IIa*, the spectrum of which shows a band  $\nu(\text{C}=\text{O})\ 1660\text{ cm}^{-1}$ , and the compound *IIb* without carbonyl,  $\nu(\text{N}-\text{H})\ 3200\text{ cm}^{-1}$ . The derivatives *IIa* and *IIb* were denoted as 6-nitro-1,2-dimethyl-3-indazolinone and 6-nitro-3-methoxy-1*H*-indazole, respectively. The both substances were prepared by two alternative routes<sup>9</sup>. The formation of two products *IIa* and *IIb* is surprising, because diazomethane usually reacts faster with enols of the type *B* at oxygen atom than with an N-acid like the lactam tautomeric form of the nitro derivative *II*. The compound *I* gives 3-methoxy-1*H*-indazole under similar conditions<sup>3</sup>. Although the reaction mixture contained excess of diazomethane, the derivative *IIb* was not alkylated at nitrogen in 1-position. Alkylation of the nitro compound *II* with dimethyl sulphate in pyridine gave only the dimethyl derivative *IIa*, whereas in 10% NaOH it gave besides *IIa* a further isomeric less polar substance not containing carbonyl and NH group. It was denoted as 6-nitro-1-methyl-3-methoxy-1*H*-indazole (*IIc*) (Table II).

Acetylation of 3-indazolinones *I-IV* with acethanhydride was used for preparation of 1-acetyl-3-acetoxy-1*H*-indazole (*V*) (see ref.<sup>10</sup>), 6-nitro- (*VI*), 5-nitro (*VII*), and 6-acetylamino-1-acetyl-3-acetoxy-1*H*-indazole (*VIII*). Ref.<sup>11</sup> gives wrongly the structure of 5-nitro-1-acetyl-3-indazolinone for the derivative *VII*. The two absorption bands in the carbonyl region at about  $1720$  and  $1770\text{ cm}^{-1}$  were assigned to 1-acetyl group and 3-acetoxy carbonyl group, respectively. The structures of the compounds *V* to *VIII* are in accord also with very intensive band  $\nu(\text{C}-\text{O})$  at  $1200\text{ cm}^{-1}$ . Partial hydrolysis<sup>10</sup> of the compound *V* gave 1-acetyl-3-indazolinone (*IX*). Similarly 6-nitro- (*X*), 5-nitro- (*XI*), and 6-acetylamino-1-acetyl-3-indazolinone (*XII*) were prepared from the diacetyl derivatives *VI* to *VIII*, respectively. The two absorption bands in the carbonyl region of IR spectra of the 1-acetyl derivatives *IX* to *XII* measured as solids were assigned to carbonyl of the lactam form *A* ( $1660\text{ cm}^{-1}$ ) and to the acetyl group bound to 1-nitrogen atom ( $1686-1704\text{ cm}^{-1}$ ) (Table II). Characteristic band  $\omega(\text{OH})$  at about  $820\text{ cm}^{-1}$  of medium intensity indicates that the studied monoacetyl derivatives are mixtures of the both tautomers type *A* and *B*.

For determination of the tautomer content we used 1-acetyl- (*IX*) and 1-acetyl-6-nitro-3-indazolinone (*X*). In the measurements we included also 1-methyl-3-indazolinone (*XIII*) (which was studied quantitatively by Janssen<sup>2</sup>), and, as a standard for calculations, 2-benzyl-3-indazolinone (*XIV*) with the fixed lactam structure *A*. From the extinction values of the absorption band  $\nu(\text{C}=\text{O})\ 1620-1698\text{ cm}^{-1}$  we calculated the content of the both tautomeric forms in solid state and in solu-



- II*, X = 6-NO<sub>2</sub>, R<sup>1</sup> = R<sup>2</sup> = H  
*IIa*, X = 6-NO<sub>2</sub>, R<sup>1</sup> = R<sup>2</sup> = CH<sub>3</sub>  
*III*, X = 5-NO<sub>2</sub>, R<sup>1</sup> = R<sup>2</sup> = H  
*IV*, X = 6-NH<sub>2</sub>, R<sup>1</sup> = R<sup>2</sup> = H  
*IX*, X = R<sup>2</sup> = H, R<sup>1</sup> = COCH<sub>3</sub>  
*X*, X = 6-NO<sub>2</sub>, R<sup>1</sup> = COCH<sub>3</sub>, R<sup>2</sup> = H  
*XI*, X = 5-NO<sub>2</sub>, R<sup>1</sup> = COCH<sub>3</sub>, R<sup>2</sup> = H  
*XII*, X = 6-NHCOCH<sub>3</sub>, R<sup>1</sup> = COCH<sub>3</sub>, R<sup>2</sup> = H  
*XIII*, X = R<sup>2</sup> = H, R<sup>1</sup> = CH<sub>3</sub>  
*XIV*, X = R<sup>1</sup> = H, R<sup>2</sup> = CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>



- IIb*, X = 6-NO<sub>2</sub>, R<sup>1</sup> = H, R<sup>2</sup> = CH<sub>3</sub>  
*IIc*, X = 6-NO<sub>2</sub>, R<sup>1</sup> = R<sup>2</sup> = CH<sub>3</sub>  
*V*, X = H, R<sup>1</sup> = R<sup>2</sup> = COCH<sub>3</sub>  
*VI*, X = 6-NO<sub>2</sub>, R<sup>1</sup> = R<sup>2</sup> = COCH<sub>3</sub>  
*VII*, X = 5-NO<sub>2</sub>, R<sup>1</sup> = R<sup>2</sup> = COCH<sub>3</sub>  
*VIII*, X = 6-NHCOCH<sub>3</sub>, R<sup>1</sup> = R<sup>2</sup> = COCH<sub>3</sub>

tions (2-propanol, chloroform, dimethyl sulphoxide, tetrahydrofuran). From the results in Table III it is obvious that the maximum content of the lactam form is present in the solutions of 2-propanol due to stabilization of the carbonyl group by solvation (hydrogen bonds). Chloroform has a substantially smaller stabilizing effect, whereas dimethyl sulphoxide and tetrahydrofuran (electron donors) stabilize rather the lactim form *B*. Electron-donating or -withdrawing effects of methyl, acetyl, and nitro groups operate according to expectation. Methyl group stabilizes the form *A* in the solvents solvating rather the carbonyl oxygen atom. Acetyl and nitro groups stabilize the form *B* in basic solvents by increasing acidity of 3-hydroxy group.

Structure of the dyestuff formed from 3-indazolinone (*I*) was described by Jennen<sup>12</sup> (resonance formulas *XVA* and *XVB*) and by Chernokalskii and coworkers<sup>13</sup> (resonance

formula *XVC*) as 2-(*N,N*-diethyl-*p*-benzoquinonediimine)indazolin-3-one (*XV*). By similar reactions we prepared 6-nitro- (*XVI*), 5-nitro- (*XVII*), and 6-amino-2-(*N,N*-diethyl-*p*-benzoquinonediimine)indazolin-3-one (*XVIII*).

TABLE III  
Solvent Effects on Tautomeric Equilibrium of 1-Substituted 3-Indazolinones

| Sample              | $\nu(\text{C}=\text{O})$ |       | E     | % C=O |
|---------------------|--------------------------|-------|-------|-------|
|                     | 1-acetyl                 | 3-oxo |       |       |
| 2-Propanol          |                          |       |       |       |
| <i>IX</i>           | 1 718                    | 1 665 | 0.301 | 51.5  |
| <i>X</i>            | 1 710                    | 1 640 | 0.275 | 47.1  |
| <i>XIII</i>         | —                        | 1 678 | 0.501 | 85.6  |
| <i>XIV</i>          | —                        | 1 680 | 0.585 | 100   |
| Chloroform          |                          |       |       |       |
| <i>IX</i>           | 1 715                    | 1 640 | 0.177 | 16.9  |
| <i>X</i>            | 1 690                    | 1 653 | 0.127 | 12.3  |
| <i>XIII</i>         | —                        | 1 660 | 0.182 | 17.4  |
| <i>XIV</i>          | —                        | 1 679 | 1.046 | 100   |
| Dimethyl Sulphoxide |                          |       |       |       |
| <i>IX</i>           | 1 700                    | 1 679 | 0.214 | 16.8  |
| <i>X</i>            | 1 706                    | 1 676 | 0.157 | 11.8  |
| <i>XIII</i>         | —                        | 1 682 | 0.206 | 15.8  |
| <i>XIV</i>          | —                        | 1 668 | 1.301 | 100   |
| Tetrahydrofurane    |                          |       |       |       |
| <i>IX</i>           | 1 720                    | 1 670 | 0.154 | 11.7  |
| <i>X</i>            | 1 718                    | 1 685 | 0.136 | 10.4  |
| <i>XIII</i>         | —                        | 1 698 | 0.121 | 9.3   |
| <i>XIV</i>          | —                        | 1 684 | 1.301 | 100   |
| Nujol <sup>a</sup>  |                          |       |       |       |
| <i>IX</i>           | 1 715                    | 1 625 | 0.155 | 10.7  |
| <i>X</i>            | 1 695                    | 1 660 | 0.150 | 10.1  |
| <i>XIII</i>         | —                        | 1 620 | 0.143 | 8.1   |
| <i>XIV</i>          | —                        | 1 637 | 1 760 | 100   |

<sup>a</sup> Approximative values.



TABLE IV  
Wave Numbers (in  $\text{cm}^{-1}$ ) in Spectra of Dyestuffs *XV*–*XVIII*

| Sample <sup>a</sup>           | X                 | $\delta(\text{N}=\text{N})^{(-)}$ | $\nu(\text{N}=\text{N})^{(-)}$ | $\nu(\text{C}=\text{N}=\text{N})$ | $\nu(\text{C}=\text{N})$ | $\nu(\text{C}=\text{N})$ | $\nu(\text{C}=\text{O})$ |
|-------------------------------|-------------------|-----------------------------------|--------------------------------|-----------------------------------|--------------------------|--------------------------|--------------------------|
| <i>XV</i>                     | H                 | 583 m                             | 1 055 vs                       | 1 144 vs                          | 1 285 s                  | 1 601 vs                 | 1 652 vs                 |
| [ <sup>15</sup> N]- <i>XV</i> | H                 | 584 m                             | 1 040 vs                       | 1 144 vs                          | 1 285 s                  | 1 602 vs                 | 1 652 vs                 |
| <i>XV</i> <sup>b</sup>        | H                 | —                                 | 1 042 vs                       | 1 142 vs                          | 1 285 vs                 | 1 599 vs                 | 1 652 vs                 |
| <i>XV</i> -HCl <sup>b</sup>   | H                 | —                                 | 1 038 s                        | 1 135 s                           | 1 282 s                  | 1 602 s                  | —                        |
| <i>XVI</i>                    | 6-NO <sub>2</sub> | 590 w, sh                         | 1 068 vs                       | 1 135 s                           | 1 273 s                  | 1 598 s                  | 1 673 s                  |
| <i>XVII</i>                   | 5-NO <sub>2</sub> | 588 w, sh                         | 1 069 vs                       | 1 144 s                           | 1 278 m                  | 1 600 vs                 | 1 668 vs                 |
| <i>XVIII</i>                  | 6-NH <sub>2</sub> | 596 m                             | 1 070 vs                       | 1 138 vs                          | 1 285 s                  | 1 590 vs                 | 1 625 vs                 |

<sup>a</sup> In carbon disulphide (400–900  $\text{cm}^{-1}$ ), in tetrachloromethane 900–1 800  $\text{cm}^{-1}$ ; for intensities see footnote <sup>a</sup> in Table I; <sup>b</sup> in Nujol.

N=N<sup>(+)</sup> in 2-position of the heterocyclic ring. Therefore, we suppose that the structures *A* and *B* (see ref.<sup>12</sup>) will be less important for stabilization of the resonance hybrid. The presence of carbonyl and N=N<sup>(-)</sup> and N=N= bonds indicates that the electron distribution in the molecule of the dyestuff *XV* is better expressed by the structure *C*. Our attempts of preparation of similar dyestuffs from 1-methyl-*(XIII)* and 2-benzyl-3-indazolinone (*XIV*) failed, only oxidation products of N,N-diethyl-1,4-diaminobenzene being isolated. <sup>1</sup>H-NMR spectrum of the dyestuff *XV* consists of a multiplet between 2.70 and 2.25 $\tau$  which can be assigned to the ABCD system of the protons of 3-indazolinone nucleus. The four protons of the quinoid nucleus form an AA', BB' system with the multiplets centered at 3.36 and 1.56 $\tau$ . The both ethyl groups are magnetically equivalent giving a quartet at 6.55 $\tau$  and a triplet at 8.80 $\tau$  with the coupling constant  $J = 6.5$  Hz. These findings agree with those of our IR spectral studies and indicate a greater contribution of the structure *XVC* for the stabilization of the resonance hybrid of the dyestuff *XV*.

## EXPERIMENTAL

The melting points were determined with a Koffler apparatus. Samples for analyses and spectral measurements were dried in vacuum of oil pump over phosphorus pentoxide for 24 hours. IR spectra were measured with a UR 20 spectrophotometer (Zeiss, Jena), the wave numbers were calibrated with polystyrene. The electronic spectra were measured with a Unicam SP 800 spectrophotometer, and the <sup>1</sup>H-NMR spectrum was measured with a Tesla BS 487 A apparatus at 80 MHz in deuteriochloroform with hexachloromethylsiloxane as the internal standard.



Exchange of hydrogen by deuterium was carried out by crystallization of 0.2 g *I* from 99.9%  $^2\text{H}_2\text{O}$  under dry nitrogen. The procedure was repeated three times to give sufficient deuteration degree according to IR spectrum.

[2- $^{15}\text{N}$ ]-3-Indazolinone was prepared from 1.64 g anthranilic acid and 1 g potassium [ $^{15}\text{N}$ ]-nitrite. Yield 0.8 g (61%), m.p. 249–250°C, ref.<sup>14</sup> gives m.p. 250–252°C.

#### Methylation of 6-Nitro-3-indazolinone (*II*)

a) Slight excess of diazomethane in ether was added portionwise to solution of 2.6 g (0.2 mol) *II* in 25 ml methanol at 0–5°C. After 30 minutes ether and most methanol were distilled off, the precipitated product was collected by suction and dried. Two fractions were separated on an alumina column (Reanal II) with benzene as eluent. The upper fraction gave, after distilling off benzene and after two crystallizations from methanol, 1.8 g (45%) orange needles, m.p. 219.5 to 220°C (*Ila*) (ref.<sup>10</sup> gives m.p. 217°C); the lower fraction gave by the same procedure 1.5 g (39.5%) yellow crystals, m.p. 211.5–212°C (*Ilb*) (ref.<sup>10</sup> gives m.p. 200°C). For *Ila*  $\text{C}_9\text{H}_9\text{N}_3\text{O}_3$  (207.9) calculated: 20.28% N; found: 20.69% N. For *Ilb*  $\text{C}_8\text{H}_7\text{N}_3\text{O}_3$  (193.2) calculated: 21.76% N; found: 21.90% N.

b) Excess of dimethyl sulphate was added in three portions to 1.8 g (0.01 mol) *II* in 25 ml pyridine at 10°C. After 24 hours standing at 20°C the mixture was diluted with 250 ml water, and the product was extracted in ethyl acetate. After distilling off the solvent the evaporation residue was crystallized from methanol to give 1.6 g (80%) yellow needles of the compound *Ila*, m.p. 219–220°C.

c) Two 50 ml portions of dimethyl sulphate were added to solution of 1.8 g (0.01 mol) *II* in 200 ml 10% NaOH with shaking and cooling with water at 15°C during 20 minutes. The solution remained alkaline during the procedure; after 10 minutes red-orange crystals of the product began to separate. After 4 hours standing at 5°C the separated product was collected by suction, washed with water until neutral, and dried over phosphorus pentoxide. Paper chromatography (Whatman No 3 impregnated with 20% formamide; benzene as eluent) showed two spots  $R_F$  0.90 and 0.39. The product was separated on an alumina column (activity I) with benzene as eluent. The first fraction was evaporated, and the residue twice crystallized from methanol gave 0.8 g (40%) yellow needles of the dimethyl derivative *Iic*, m.p. 165–165.5°C. For  $\text{C}_9\text{H}_9\text{N}_3\text{O}_3$  (207.2) calculated: 20.28% N; found: 20.07% N. The column was extracted with ethyl acetate to give the second fraction which gave, after two crystallizations from methanol, 1.1 g (54.5%) orange needles; according to mixed melting point and IR spectrum this product was identical with the compound *Ila*.

#### Acetyl Derivatives

Preparation and hydrolysis of 1-acetyl-3-acetoxy-1*H*-indazoles *V*–*VIII* was carried out as those of *V* (ref.<sup>11</sup>). In hydrolysis of 5-nitro derivative *VII* 0.3 g *p*-toluenesulfonic acid was used as catalyst, and the product was isolated after concentration of the mixture *in vacuo*. The results are given in Table V.

#### Dyestuffs *XV*–*XVIII*

The dyestuffs were prepared by oxidation of the mixture of the respective 3-indazolinones *I*–*IV* (0.01 mol) and *N,N*-diethyl-1,4-diaminobenzene with silver chloride in water with addition

TABLE V  
Acetyl Derivatives of Substituted 1*H*-Indazoles and 3-Indazolinones

| Derivative | M.p., °C<br>(yield, %)       | Formula<br>(mol.wt.)   | Calculated/Found |      |       |
|------------|------------------------------|--|------------------|------|-------|
|            |                              |  | % C              | % H  | % N   |
| VI         | 147–148<br>(83)              | C <sub>11</sub> H <sub>9</sub> N <sub>3</sub> O <sub>5</sub><br>(263·2)  | 50·20            | 3·45 | 15·96 |
|            |                              |  | 49·73            | 3·59 | 15·97 |
| VII        | 162–163<br>(76)              | C <sub>11</sub> H <sub>9</sub> N <sub>3</sub> O <sub>5</sub><br>(263·2)  | 50·20            | 3·45 | 15·96 |
|            |                              |  | —                | —    | 15·52 |
| VIII       | 191–193<br>(80)              | C <sub>13</sub> H <sub>13</sub> N <sub>3</sub> O <sub>4</sub><br>(275·3) | 56·72            | 4·76 | 15·26 |
|            |                              |  | 56·62            | 4·94 | 15·60 |
| X          | 236–238<br>(81)              | C <sub>9</sub> H <sub>7</sub> N <sub>3</sub> O <sub>4</sub><br>(221·2)   | 48·87            | 3·19 | 19·00 |
|            |                              |  | 48·69            | 3·43 | 19·20 |
| XI         | 238–239 <sup>a</sup><br>(55) | —  | —                | —    | —     |
| XII        | 280–285<br>(78)              | C <sub>11</sub> H <sub>11</sub> N <sub>3</sub> O <sub>3</sub><br>(233·2) | 56·65            | 7·45 | 18·02 |
|            |                              |  | 56·26            | 7·01 | 17·74 |

<sup>a</sup> Ref. <sup>11</sup> gives m.p. 239°C.

of sodium carbonate<sup>13</sup>. After filtration the dyestuffs were extracted with ethyl acetate, the combined extracts were dried with anhydrous sodium sulphate, and the solvent was distilled off *in vacuo*. The dyestuff was isolated by column chromatography on alumina activity II with acetone as eluent. Melting points and electronic spectra of the dyestuffs XV and XVI agreed with literature data<sup>12,13</sup>. Melting point of the dyestuff XVIII was 236–237°C,  $\lambda_{\max}$  547 nm,  $\log \epsilon$  4·55 (ethanol),  $\nu(\text{N—H})$  3280 and 3400  $\text{cm}^{-1}$  (tetrachloromethane).

*Elemental analyses were carried out in Analytical Chemistry Department, Institute of Chemical Technology Pardubice, under the guidance of Dr J. Bulušek. The authors are indebted to Dr V. Macháček, Organic Chemistry Department, for interpretation of <sup>1</sup>H-NMR spectra, and to Mrs J. Metlická from the same Department for technical assistance.*

#### REFERENCES

- O'Sullivan S. S.: *J. Chem. Soc.* 1960, 3278.
- Janssen R.: *Advances in Molecular Spectroscopy*, p. 820. Pergamon Press, Oxford 1962; *Chem. Abstr.* 59, 8865 (1963).
- Evans N. A., Whelan D. J., Johns R. B.: *Tetrahedron* 21, 3351 (1965).
- Schiedt W.: *Angew. Chem.* 66, 609 (1954).
- Dudek G. O., Dudek E. P.: *J. Amer. Chem. Soc.* 88, 2407 (1966).
- Kübler R., Lüttke W., Weckherlin S.: *Z. Elektrochem.* 64, 650 (1960).

7. Bassignana P., Cogrossi C.: *Tetrahedron* 20, 2361 (1964).
8. Mashima M.: *Bull. Soc. Chem. Jap.* 35, 2020 (1962).
9. Arold H.: *J. Prakt. Chem.* 25, 18 (1964).
10. Meisenheimer J., Diedrich A.: *Ber.* 57, 1715 (1924).
11. Kenner J., Witham E.: *J. Chem. Soc.* 119, II, 1055 (1921).
12. Jennen J.: U.S. 2 673 801; *Chem. Abstr.* 48, 9850 (1954).
13. Chernokalskii B. D., Groyberg A. T., Berdenezhnaya A. R.: *Khim. Geterocikl. Soedin. Akad. Nauk. Latv. SSR* 1965 (3), 412; *Chem. Abstr.* 63, 16332 (1965).
14. Stephenson E.: *Org. Syntheses*, Coll. Vol. III, 475 (1955).

Translated by J. Panchartek.