# Ring contraction in reactions of 3-benzoylquinoxalin-2-ones with 1,2-phenylenediamines. Quinoxaline-benzoimidazole rearrangement*

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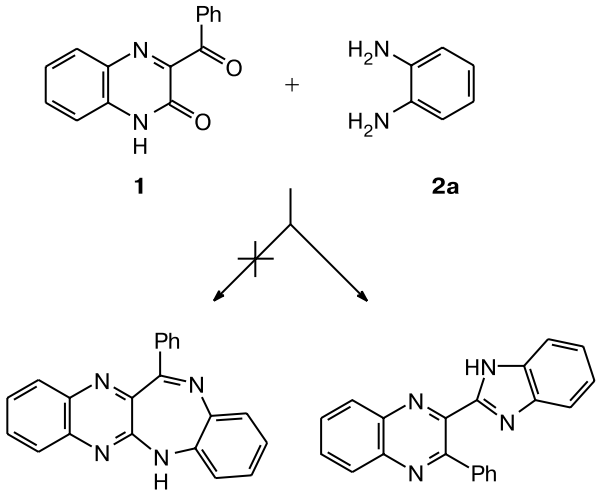
The reactions of 3-benzoylquinoxalin-2-one and its *N*(1)-alkyl derivatives with 1,2-phenylenediamines were accompanied by ring contraction as a result of the quinoxaline-benzoimidazole rearrangement giving rise to 2-benzoimidazolyl-substituted quinoxalines. The possible pathways of these reaction are discussed.

**Key words:** 3-benzoylquinoxalin-2-ones, 1,2-phenylenediamines, benzoimidazole, pyrazine-imidazole ring contraction, rearrangements, IR spectra, $^1$H NMR spectra, X-ray diffraction analysis.

The presence of several closely-spaced electrophilic and nucleophilic centers in readily available[2,3] polyfunctional ketone of the quinoxaline series, *viz.*, 3-benzoyl-2-oxo-1,2-dihydroquinoxaline (**1**), is responsible for its unpredictable behavior with respect to multicenter reagents due to which compound **1** can be involved in unexpected reactions.

The present study was aimed at establishing the structures of compounds produced in the reactions of ketone **1** and its *N*(1)-alkyl derivatives with 1,4-binucleophiles, *viz.*, *o*-phenylenediamine (*o*-PDA, **2a**), 4-nitro-1,2-phenylenediamine (**2b**), and 3,4-diaminotoluene (**2c**), and elucidating possible pathways of their formation. By analogy with the reactions with 1,2-binucleophiles (hydrazine, arylhydrazines, and thiosemicarbazide) in refluxing AcOH giving rise to annelation products, *viz.*, pyrazolo[3,4-*b*]quinoxalines (flavazoles),[4] the reaction of ketone **1** with *o*-PDA would be expected to form quinoxalino[2,3-*b*]benzo-1,5-diazepine system **3**. Actually, the reaction performed under these conditions involved condensation accompanied by elimination of two water molecules to give a product with composition $C_{21}H_{14}N_4$. However, this reaction did not produce expected quinoxalinobenzodiazepine **3**. Although the IR and $^1$H NMR spectra of the reaction product do not contradict structure **3**, this compound cannot give the observed $^{13}$C NMR spectrum, in which 21 carbon atoms appear as 19 signals, six of which are broadened. This $^{13}$C NMR spectral pattern can be assigned, for example, to the isomer of quinoxalinobenzodiazepine **3**, *viz.*, benzoimidazolylquinoxaline **4**, in which benzoimidazole prototropy leads to broadening of the signals for six carbon atoms of the benzo fragment of the benzoimidazole system[1] (Scheme 1).

**Scheme 1**




* For the preliminary communication, see Ref. 1.

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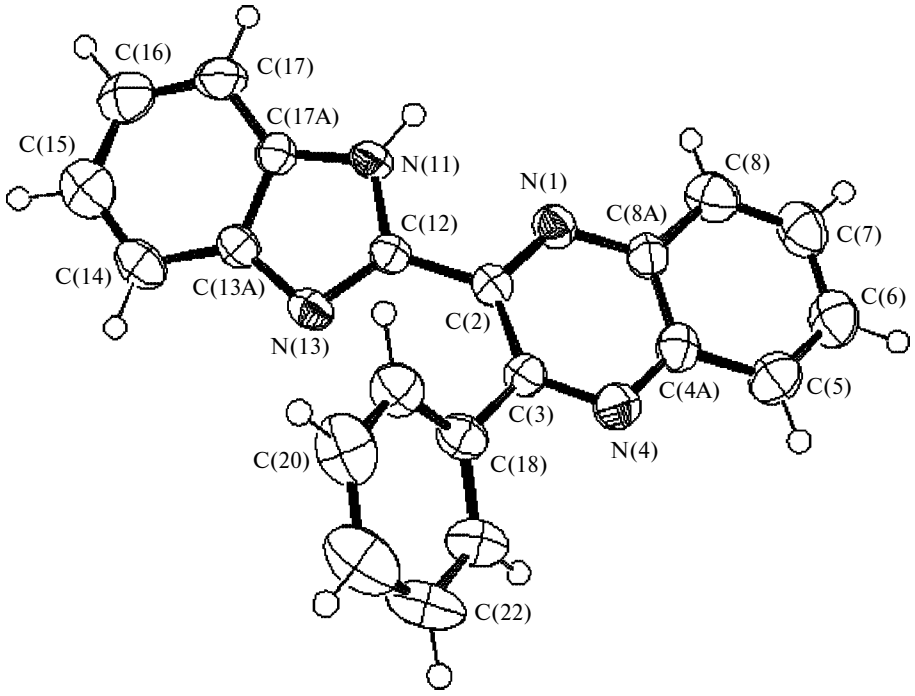



**Fig. 1.** Molecular structure of compound **4** in the crystal.

The above assumption was confirmed by the results of X-ray diffraction analysis of this compound, according to which it has the structure of 2-(benzoimidazol-2′-yl)-3-phenylquinoxaline (**4**). Compound **4** crystallizes in the monoclinic system with one molecule per asymmetric unit (Fig. 1). The quinoxaline and benzoimidazole fragments of the molecule are planar within the experimental error (0.05(1) and 0.01(1) Å, respectively). The dihedral angle between these planes is 26.58(6)°. The dihedral angle between the planes of the Ph substituent and the quinoxaline fragment is 40.30(8)°. In the crystal, the molecules are linked in infinite chains along the crystallographic axis 0*x* *via* intermolecular N—H...N hydrogen bonds ($d$(H(1)...N(21′)), 2.20(1) Å; N(10)—H(1)...N(21′), 158.6(2)°; the symmetry operation $1/2 + x$, $1/2 - y$, $1/2 + z$).

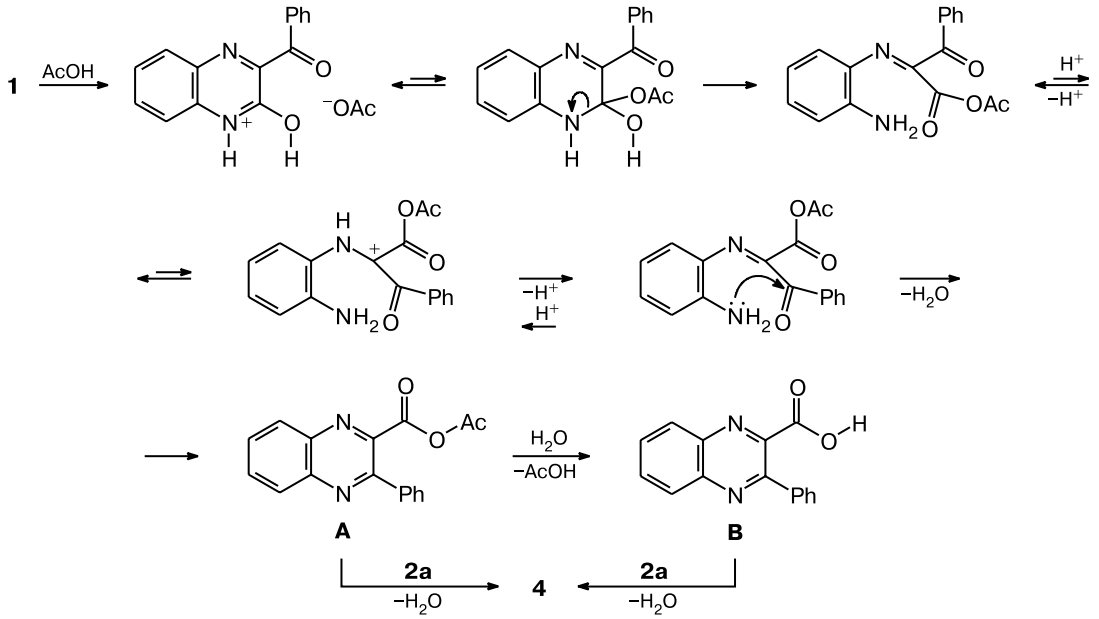
The carbon fragment Ph—C—C—C of the starting benzoylquinoxalinone **1** is completely transferred to compound **4** with insertion into the structures of both the phenyl-substituted quinoxaline ring that formed and the newly constructed benzoimidazole ring. Hence, the C(2) atom in the latter should correspond to the C(2) atom in the starting quinoxalinone (pyrazinone) ring. This implies that the quinoxaline-benzoimidazole rearrangement is accompanied by the quinoxaline-ring contraction; the benzoimidazole ring is built from *o*-PDA and one of the pyrazine C atoms of the starting quinoxalinone system. The new phenylpyrazine ring is constructed through the insertion of the ketone C atom of the benzoyl group into the ring. This reaction falls under the most general definition of molecular rearrangements as chemical reactions associated with a change in the sequence of bonds (molecular skeleton) and violation of the principle of minimum structural changes.[5]

The reaction can follow several pathways. In particular, it can be assumed that benzoylquinoxalinone **1** (like, for example, its oxygen analog, *viz.*, 3-formyl-2-phenylbenzo-1,4-dioxine[6]) undergoes recyclization under the action of AcOH as a result of the ring-chain transformation through an unstable open-chain form. In the latter, the intramolecular addition of the amino group occurs at the more reactive carbonyl group of the benzoyl fragment through the intermediate formation of mixed anhydride **A**. Hence, the formation of final product **4** can be represented as the Phillips—Landenburg reaction[7] of *o*-PDA **2a** with either anhydride **A** or a product of its hydrolysis, *viz.*, 3-phenylquinoxaline-2-carboxylic acid **B** (Scheme 2).

However, this sequence of reactions cannot be responsible for the quinoxaline-benzoimidazole rearrangement and the formation of compound **4**, because the starting compound in the reactions of benzoylquinoxalinone **1** with acetic, hydrochloric, and sulfuric acids at different concentrations and at different temperatures almost always remained unconsumed and, consequently, the quinoxaline-quinoxaline recyclization did not take place.

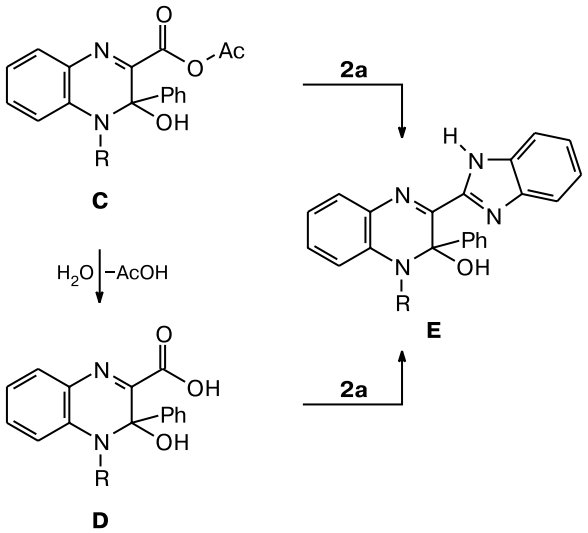
To conclusively exclude the possibility of the reaction occurring through the quinoxaline-quinoxaline recyclization according to Scheme 2, we studied the behavior of

**Scheme 2**



*N*(1)-alkylated derivatives of benzoylquinoxalinone **5—10** with respect to *o*-PDA in refluxing AcOH in the expectation that (regardless of the *N*(1)-alkylated derivative of quinoxaline used) this rearrangement giving rise to the final products through the intermediates **C** and **D** would afford products **E** 2-hydroxy-*N*-alkylated at the quinoxaline N(1) atom (Scheme 3).

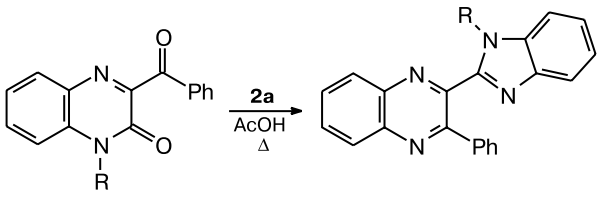
**Scheme 3**



Compounds **5—9** were prepared by alkylation of 3-benzoylquinoxalinone **1** with alkyl iodides. Compound **10** was synthesized by alkylation with benzyl chloride under standard conditions[8] (in refluxing dioxane in the presence of KOH). The structures of compounds **5—10** were proved by elemental analysis data, the fact that the IR spectra of the products retain vibrational frequencies of the lactam carbonyl group at 1670—1685 $cm^{-1}$, and the fact that the $^1H$ NMR spectra do not show a broadened singlet at very low field (δ 12.92) corresponding to the proton at the N atom in the starting compound **1** (Tables 1 and 2).

Condensation of *N*(1)-alkyl or benzyl derivatives **5—10** of 3-benzoyl-2-oxo-1,2-dihydroquinoxaline (**1**) with *o*-PDA in refluxing AcOH proceeded smoothly and afforded crystalline products in high yields. The compositions of these products correspond to *N*(1)-substituted benzoimidazolylquinoxalines **11—16**, whose IR spectra have no absorption bands of carbonyl groups (Scheme 4, Tables 1 and 2). In the $^1H$ NMR spectra, the multiplicities of the signals for the protons of the benzo fragments

**Scheme 4**



**5—10** **11—16**

R = Me (**5**, **11**), Et (**6**, **12**), $Pr^n$ (**7**, **13**), $Bu^n$ (**8**, **14**), *n*-$C_5H_{11}$ (**9**, **15**), $PhCH_2$ (**10**, **16**)

**Table 1.** Characteristics of compounds **5—19**

| Compound | M.p. /°C | Yield (%) | Found / Calculated (%) | | | Molecular formula |
|---|---|---|---|---|---|---|
| | | | C | H | N | |
| **5** | 151—153 | 54 | 72.80 | 4.67 | 10.56 | $C_{16}H_{12}N_2O_2$ |
| | (MeOH) | | 72.72 | 4.58 | 10.60 | |
| **6** | 101—103 | 66 | 73.56 | 4.89 | 10.31 | $C_{17}H_{14}N_2O_2$ |
| | ($Pr^iOH$) | | 73.37 | 5.07 | 10.07 | |
| **7** | 83—85 | 68 | 73.79 | 5.87 | 9.56 | $C_{18}H_{16}N_2O_2$ |
| | ($Pr^iOH$) | | 73.95 | 5.52 | 9.58 | |
| **8** | 103—105 | 57 | 74.40 | 6.06 | 9.35 | $C_{19}H_{18}N_2O_2$ |
| | (MeOH) | | 74.49 | 5.92 | 9.14 | |
| **9** | 95—98 | 58 | 74.87 | 6.52 | 8.78 | $C_{20}H_{20}N_2O_2$ |
| | (MeOH) | | 74.98 | 6.29 | 8.74 | |
| **10** | 126—128 | 54 | 77.59 | 4.55 | 8.26 | $C_{22}H_{16}N_2O_2$ |
| | (MeOH) | | 77.63 | 4.74 | 8.23 | |
| **11** | 186—188 | 81 | 78.36 | 4.67 | 16.56 | $C_{22}H_{16}N_4$ |
| | (MeOH) | | 78.55 | 4.79 | 16.66 | |
| **12** | 117—119 | 79 | 78.66 | 5.03 | 16.26 | $C_{23}H_{18}N_4$ |
| | ($Pr^iOH$) | | 78.83 | 5.18 | 15.99 | |
| **13** | 166—168 | 87 | 79.38 | 5.37 | 15.39 | $C_{24}H_{20}N_4$ |
| | ($Pr^iOH$) | | 79.10 | 5.53 | 15.37 | |
| **14** | 105—107 | 87 | 79.56 | 5.89 | 15.08 | $C_{25}H_{22}N_4$ |
| | (MeOH) | | 79.34 | 5.86 | 14.80 | |
| **15** | 65—67 | 86 | 79.33 | 6.08 | 14.47 | $C_{26}H_{24}N_4$ |
| | (MeOH) | | 79.56 | 6.16 | 14.27 | |
| **16** | 150—153 | 56 | 81.50 | 4.79 | 13.63 | $C_{28}H_{20}N_4$ |
| | (MeOH) | | 81.53 | 4.89 | 13.58 | |
| **17a** | 246—248 | 39 | 68.99 | 3.15 | 19.03 | $C_{21}H_{13}N_5O_2$ |
| | (DMSO) | | 68.86 | 3.30 | 19.12 | |
| **17b** | 321—324 | 44 | 68.94 | 3.35 | 19.06 | $C_{21}H_{13}N_5O_2$ |
| | (DMSO) | | 68.86 | 3.30 | 19.12 | |
| **18** | 216—218 | 81 | 67.61 | 3.78 | 16.95 | $C_{23}H_{15}N_5O_3$ |
| | | | 67.48 | 3.69 | 17.11 | |
| **19** | 262—278 | 82 | 78.86 | 4.79 | 16.58 | $C_{22}H_{16}N_4$ |
| | (DMSO) | | 78.79 | 4.51 | 16.71 | |

and the Ph group of compounds **11—16** are analogous to those observed in the spectrum of compound **4** (see Table 2), *i.e.*, *N*-substitution does not hinder the quinoxaline-benzoimidazole rearrangement.

X-ray diffraction analysis of methyl homolog **11** confirmed its structure. Compound **11** crystallizes in the triclinic system with one independent molecule per asymmetric unit (Fig. 2). The quinoxaline and benzoimidazole rings in molecule **11** are planar to within the experimental error (0.03(2) and 0.01(1) Å, respectively). The dihedral angle between these planes is 64.7(2)°. The dihedral angle between the Ph substituent and the plane of the quinoxaline fragment is 48.9(2)°. This mutual arrangement does not hinder the formation of an intramolecular C—H...N contact between the H(23) proton of the Ph substituent and the N(4) atom (H(23)...N(4), 2.70(2) Å).

The molecular packing in the crystal of **11** is determined by weak intermolecular C—H...N, C—H...π, and π—π interactions. The interactions between the electron systems of the quinoxaline fragments of the molecules related to each other by a translation along the axis 0*x* give rise to tilted stacks of the molecules extended along the crystallographic axis (the shortest distance between the planes of the rings is 4.23(2) Å; the dihedral angle is 2.5(2)°) (Fig. 3). The intermolecular interactions between the H(243) protons of the methyl groups and the N(1′) atoms of the molecules related by the symmetry operation $-1 + x, y, z$ ($d$(H(243)...N(1′)), 2.64(2) Å; C(24)—H(243)...N(1′), 113.3°) are also responsible for the formation of stacks. The molecules, which are related by the center of symmetry, are involved in formation of stacks with an antiparallel orientation of the molecules through the above-mentioned interactions. These stacks are linked in a three-dimensional supramolecular structure with a rather high packing coefficient (67.7%) *via*

**Table 2.** IR and $^1$H NMR spectra of compounds **5—19**

| Compound | IR, ν/cm$^{-1}$ | $^1$H NMR, δ (*J*/Hz) (solvent) |
|---|---|---|
| **5** | 550, 600, 690, 730, 760, 940, 1160, 1180, 1260, 1320, 1450, 1470, 1560, 1595, 1640, 1670 | 3.70 (s, 3 H, Me); 7.56 (ddd, 1 H, H(6) or H(7), $J$ = 7.6, $J$ = 6.7, $J$ = 1.4); 7.66 (dd, 2 H, *m*-$H_{Ph}$, $J$ = 7.9, $J$ = 7.4); 7.74—7.92 (m, 3 H, H(6) or H(7), H(8), *p*-$H_{Ph}$); 7.91 (dd, 1 H, H(5), $J$ = 7.9, $J$ = 1.4); 8.05 (dd, 2 H, *o*-$H_{Ph}$, $J$ = 8.1, $J$ = 1.4) (DMSO-$d_6$) |
| **6** | 694, 728, 766, 827, 945, 1169, 1324, 1448, 1560, 1586, 1602, 1646, 1681 | 1.37 (t, 3 H, Me, $J$ = 7.3); 4.39 (q, 2 H, $CH_2$, $J$ = 7.3); 7.45 (ddd, 1 H, H(6) or H(7), $J$ = 8.3, $J$ = 6.1, $J$ = 2.4); 7.56 (dd, 2 H, *m*-$H_{Ph}$, $J$ = 7.3); 7.67—7.77 (m, 3 H, H(6) or H(7), H(8), *p*-$H_{Ph}$); 7.87 (dd, 1 H, H(5), $J$ = 7.7); 8.02 (dd, 2 H, *o*-$H_{Ph}$, $J$ = 7.7, $J$ = 1.6) (acetone-$d_6$) |
| **7** | 694, 729, 765, 826, 906, 959, 1170, 1255, 1321, 1342, 1561, 1601, 1648, 1681 | 0.88 (t, 3 H, Me, $J$ = 7.7); 1.79—1.95 (m, 2 H, MeC$\underline{H}_2$); 4.34 (t, 2 H, $NCH_2$, $J$ = 7.7); 7.44 (ddd, 1 H, H(6) or H(7), $J$ = 8.3, $J$ = 5.7, $J$ = 2.8); 7.56 (dd, 2 H, *m*-$H_{Ph}$, $J$ = 8.1, $J$ = 7.3); 7.67—7.77 (m, 3 H, H(6) or H(7), H(8), *p*-$H_{Ph}$); 7.87 (dd, 1 H, H(5), $J$ = 7.7); 8.02 (dd, 2 H, *o*-$H_{Ph}$, $J$ = 8.1, $J$ = 1.6) (acetone-$d_6$) |

(*to be continued*)

**Table 2** (*continued*)

| Compound | IR, ν/cm$^{-1}$ | $^1$H NMR, δ (*J*/Hz) (solvent) |
|---|---|---|
| **8** | 695, 700, 715, 1170, 1325, 1380, 1450, 1470, 1580, 1600, 1640, 1680 | 1.02 (t, 3 H, Me, *J* = 7.6); 1.45—1.63 (m, 2 H, MeC$\underline{H}_2$(CH$_2$)$_2$); 1.76—1.90 (m, 2 H, MeCH$_2$C$\underline{H}_2$CH$_2$); 4.39 (t, 2 H, Me(CH$_2$)$_3$C$\underline{H}_2$, *J* = 7.6); 7.49 (ddd, 1 H, H(6) or H(7), *J* = 7.9, *J* = 6.4, *J* = 2.1); 7.61 (ddd, 2 H, *m*-H$_{Ph}$, *J* = 7.6, *J* = 7.1, *J* = 1.5); 7.72—7.81 (m, 3 H, H(6) or H(7), H(8), *p*-H$_{Ph}$); 7.92 (dd, 1 H, H(5), *J* = 7.9, *J* = 1.4); 8.07 (dd, 2 H, *o*-H$_{Ph}$, *J* = 7.9, *J* = 1.5) (acetone-d$_6$) |
| **9** | 715, 735, 945, 1010, 1110, 1170, 1270, 1330, 1350, 1380, 1460, 1470, 1560, 1580, 1600, 1640, 1680 | 1.03 (t, 3 H, Me, *J* = 6.7); 1.42—1.65 (m, 4 H, Me(C$\underline{H}_2$)$_2$(CH$_2$)$_2$); 1.80—1.92 (m, 2 H, Me(CH$_2$)$_2$C$\underline{H}_2$CH$_2$); 4.38 (t, 2 H, Me(CH$_2$)$_3$C$\underline{H}_2$, *J* = 7.9); 7.51 (ddd, 1 H, H(6) or H(7), *J* = 7.4, *J* = 6.5, *J* = 1.1); 7.63 (dd, 2 H, *m*-H$_{Ph}$, *J* = 7.9, *J* = 7.0); 7.68—7.85 (m, 3 H, H(6) or H(7), H(8), *p*-H$_{Ph}$); 7.95 (dd, 1 H, H(5), *J* = 7.9, *J* = 1.4); 8.00 (dd, 2 H, *o*-H$_{Ph}$, *J* = 7.6, *J* = 1.40) (DMSO-d$_6$) |
| **10** | 535, 595, 725, 900, 1170, 1320, 1380, 1450, 1460, 1550, 1600, 1650, 1685 | 5.67 (s, 2 H, CH$_2$); 7.25—7.40 (m, 5 H, CH$_2$$\underline{Ph}$); 7.45 (dd, 1 H, H(6) or H(7), *J* = 7.4, *J* = 7.4); 7.56—7.82 (m, 5 H, *p*-H$_{PhCO}$, *m*-H$_{PhCO}$, H(6) or H(7), H(8)); 7.93 (dd, 1 H, H(5), *J* = 8.0, *J* = 1.1); 8.02 (d, 2 H, *o*-H$_{PhCO}$, *J* = 6.9) (DMSO-d$_6$) |
| **11** | 580, 700, 720, 750,765, 780, 990, 1005, 1075, 1085, 1135, 1215, 1340, 1380, 1450, 1470, 1550, 1615 | 3.86 (s, 3 H, Me); 7.22—7.43, 7.50—7.68, 7.92—8.08, 8.20—8.32 (all m, 5 H + 4 H + 2 H + 2H, H arom.) (DMSO-d$_6$) |
| **12** | 702, 771, 992, 1067, 1126, 1183, 1247, 1270, 1335, 1416 | 1.43 (t, 3 H, Me, *J* = 7.3); 4.44 (q, 2 H, CH$_2$, *J* = 7.3); 7.22—7.40, 7.56—7.70, 7.90—8.10, 8.15—8.28 (all m, 5 H + 4 H + 2 H + 2H, H arom.) (acetone-d$_6$) |
| **13** | 698, 751, 768, 991, 1070, 1126, 1184, 1249, 1280, 1335, 1415 | 1.04 (t, 3 H, Me, *J* =7.7); 1.75—1.90 (m, 2 H, MeC$\underline{H}_2$); 4.30 (t, 2 H, NCH$_2$, *J* = 7.7); 7.20—7.40, 7.55—7.70, 7.90—8.10, 8.15—8.30 (all m, 5 H + 4 H + 2 H + 2H, H arom.) (acetone-d$_6$) |
| **14** | 435, 550, 565, 695, 710, 750, 760, 1000, 1080, 1130, 1170, 1220, 1250, 1280, 1330, 1380, 1410, 1460, 1480, 1610 | 0.88 (t, 3 H, Me, *J* =7.6); 1.22—1.38 (m, 2 H, MeC$\underline{H}_2$(CH$_2$)$_2$); 1.73—1.90 (m, 2 H, MeCH$_2$C$\underline{H}_2$CH$_2$); 4.37 (t, 2 H, Me(CH$_2$)$_2$C$\underline{H}_2$, *J* = 7.6); 7.20—7.40, 7.55—7.68, 7.88—8.04, 8.15—8.28 (all m, 5 H + 4 H + 2 H + 2H, H arom.) (DMSO-d$_6$) |
| **15** | 560, 700, 750, 765, 1080, 1340, 1410, 1610 | 0.78 (t, 3 H, Me, *J* = 6.8); 1.10—1.32 (m, 4 H, Me(C$\underline{H}_2$)$_2$(CH$_2$)$_2$); 1.75—1.90 (m, 2 H, Me(CH$_2$)$_2$C$\underline{H}_2$CH$_2$); 4.36 (t, 2 H, Me(CH$_2$)$_2$C$\underline{H}_2$, *J* = 7.7); 7.20—7.40, 7.55—7.68, 7.88—8.04, 8.15—8.28 (all m, 5 H + 4 H + 2 H + 2H, H arom.) (acetone-d$_6$) |
| **16** | 695, 730, 760, 770, 970, 1090, 1170, 1335, 1380, 1410, 1460, 1605 | 5.69 (s, 2 H, CH$_2$); 7.02—7.46, 7.58—7.68, 7.90—8.08, 8.12—8.28 (all m, 10 H + 4 H + 2 H + 2H, H arom.) (acetone-d$_6$) |
| **17a** | 435, 650, 700, 740, 760, 840, 910, 1075, 1130, 1200, 1310, 1330, 1350, 1410, 1440, 1460, 1515, 1610, 3240—3470 | 7.34—7.60 (m, 9 H, H arom.); 8.51 (d, 1 H, H(5), *J* = 9.0); 8.72 (dd, 1 H, H(6), *J* = 9.0, *J* = 2.2); 9.06 (d, 1 H, H(8), *J* = 2.2); 13.18 (br.s, NH) (DMSO-d$_6$) |
| **17b** | 620, 700, 735, 750, 830, 1080, 1200, 1310, 1330, 1345, 1460, 1530, 1615, 3385 | 7.22—7.75 (m, 9 H, H arom.); 8.47 (d, 1 H, H(8), *J* = 8.9); 8.67 (dd, 1 H, H(7), *J* = 8.9, *J* = 2.5); 9.01 (d, 1 H, H(5), *J* = 8.9); 13.16 (br.s, NH) (DMSO-d$_6$) |
| **18** | 694, 751, 823, 984, 1047, 1100, 1146, 1199, 1262, 1307, 1431, 1532, 1541, 1623, 1719 | 1.93 (s, 3 H, Me); 7.22—7.80 (m, 7 H, Ph, H(5) and H(6) of benzoimidazole); 7.60 (d, 1 H, H(4) or H(7) of benzoimidazole, *J* = 7.6); 7.87 (d, 1 H, H(4) or H(7) of benzoimidazole, *J* = 7.6); 8.43 (d, 1 H, H(8), *J* = 9.2); 8.64 (dd, 1 H, H(7), *J* = 9.2, *J* = 2.3); 9.04 (d, 1 H, H(5), *J* = 3.0) (DMSO-d$_6$) |
| **19** | 545, 695, 755, 770, 810, 830, 1100, 1220, 1315, 1350, 1380, 1430, 1450, 1460, 1485, 1620, 2800—3400 | 7.20—7.74 (m, 9 H, H arom.); 7.88 (dd, 1 H, H(7), *J* = 8.3, *J* = 1.9); 8.08 (br.s, 1 H, H(5)); 8.18 (d, 1 H, H(6), *J* = 8.3); 8.20 (d, 1 H, H(8), *J* = 8.3); 12.99 (br.s, NH) (DMSO-d$_6$) |

numerous C—H...N and C—H...π contacts with the H...X distances varying from 4.06 to 4.48 Å.

The results of X-ray diffraction analysis unambiguously showed that the reactions of *N*-alkylated benzoylquinoxalinones with *o*-PDA are actually accompanied by the contraction of the *N*-alkylated quinoxaline ring rather than proceed through the quinoxaline-quinoxaline rearrangement.

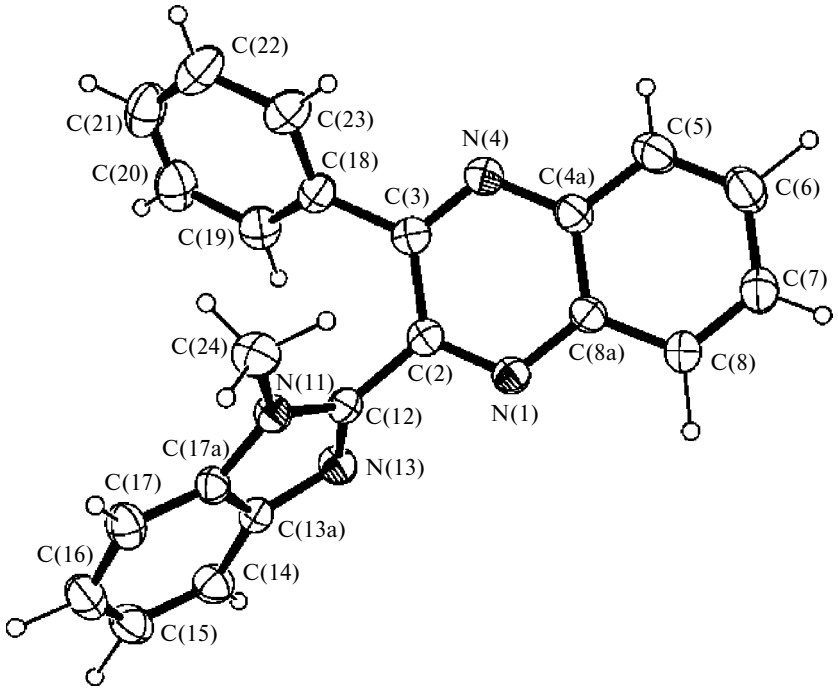



**Fig. 2.** Molecular structure of compound **11** in the crystal.

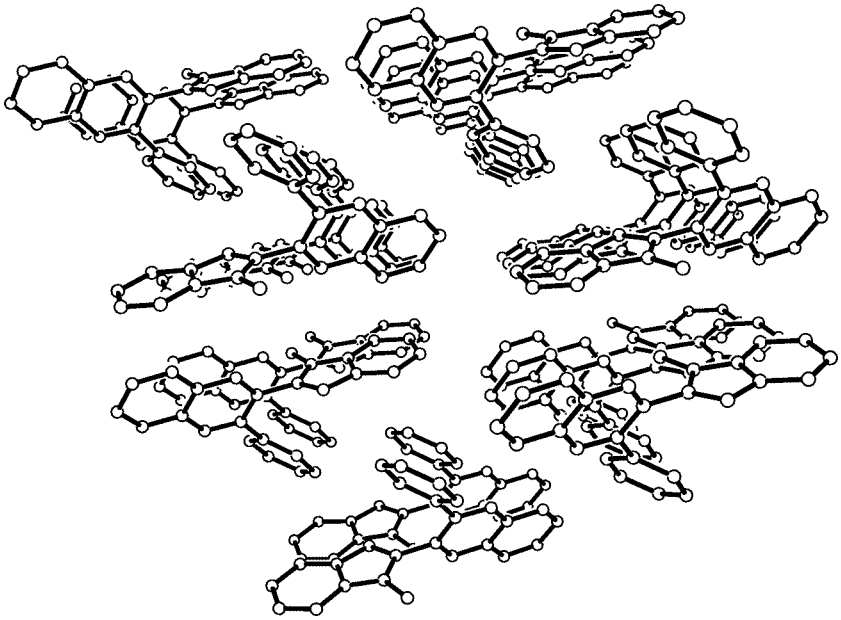
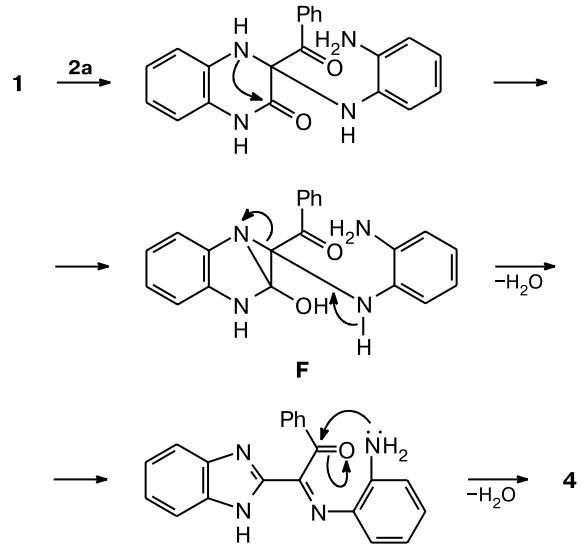


**Fig. 3.** Molecular packing of compound **11** in the crystal (H atoms are omitted) projected along the crystallographic axis 0*x*.

It can also be supposed that, like the reaction of 2,3-diphenylquinoxaline with potassium amide giving rise to 2-phenylbenzoimidazole,[9,10] the reaction of 3-benzoylquinoxalinone **1** with substantially less nucleophilic *o*-PDA involves the addition of the amino group at the C(3) atom of quinoxalinone **1** as the first step, and the ring contraction proceeds with the cleavage of the C(3)—N(4) bond in the intermediate tricyclic system **F**. The next step involves the nucleophilic attack of the second amino group at the benzoyl fragment to form (after elimination of two water molecules) the quinoxaline derivative containing the benzoimidazole fragment at position 2 (Scheme 5).

Finally, it can be suggested that the first step of the reaction involves the nucleophilic attack of the amino

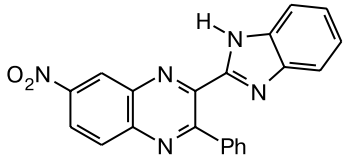
**Scheme 5**



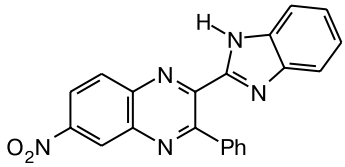
group at the benzoyl group of compound **1** followed by the attack of the second amino group at the C(3) atom of the quinoxaline system with the intermediate formation of the compound **G**. The latter can be transformed into final structure **4** following at least two pathways, *viz.*, through the intermediate compound **H** (path *A*) and the intermediate compounds **I** and **J** (path *B*) (Scheme 6).

We studied the behavior of *o*-phenylenediamines containing the $NO_2$ and Me substituents in the benzene ring, which exhibit substantially different electronic effects, in the reaction with 3-benzoyl-2-oxo-1,2-dihydroquinoxaline (**1**).

Due to the presence of the reactive benzoyl fragment in quinoxaline derivatives **5—10**, their reactions with *o*-PDA **2a** can involve the initial attack not only at the C(3) atom of the quinoxaline fragment (see Scheme 5), which has been proposed for the reactions of quinoxaline derivatives with potassium amide,[9] but also at the C atom of the carbonyl group of the benzoyl fragment. To elucidate the pathways of the reactions of benzoylquinoxalines **1** and **5—10** with *o*-PDA (with the attack of the amino group of *o*-PDA either at the C(3) atom or at the carbonyl C atom of the benzoyl group), we carried out the reaction of compound **1** with 4-nitro-1,2-phenylenediamine (**2b**) assuming that the more active second amino group (in the *meta* position with respect to the nitro group) rather than the first amino group (which is deactivated under the influence of the nitro group) is responsible for the first step of both reactions. As can be seen from Scheme 5, the reactions, which proceed with the pyrazine-ring contraction and involve the initial attack at the C(3) atom of the quinoxaline fragment, would afford compound **17a** rather than its isomer **17b** as the only or major product.

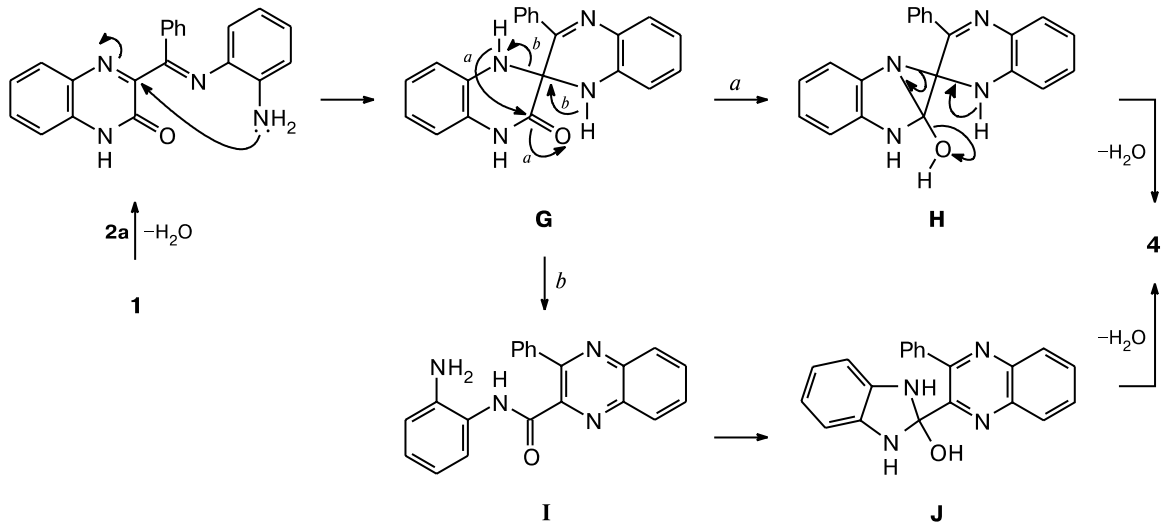


**17a**



**17b**

**Scheme 6**



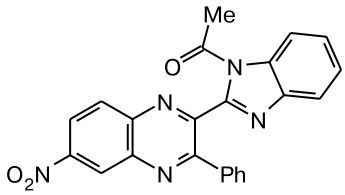
In the case of the initial attack of the amino group at the benzoyl fragment (see Scheme 6), the reaction would afford compound **17b** rather than **17a** as the major product. However, the reaction of compound **1** with diamine **2b** always gave rise to two products in virtually equal yields. These products can readily be isolated from the reaction mixture. One of these products with m.p. 321—324 °C (**17a**) precipitated in refluxing AcOH in the course of the reaction (as shown below). Another product with m.p. 246—248 °C (**17b**) was precipitated from AcOH with water. In spite of the fact that these two compounds differ substantially not only in the melting points but also in solubility, they give similar IR spectra and the signals in their $^1$H and $^{13}$C NMR spectra are virtually identical in positions and multiplicities. The NMR spectra call for more detailed investigation with the use of calculation methods and 2D NMR experiments. The results of this investigation will be published elsewhere.

Since we failed to grow crystals of either high-melting or low-melting isomers suitable for X-ray diffraction study, we analyzed the IR spectra of these compounds, which were recorded both for the condensed phase and their solutions.

As mentioned above, the spectra of both compounds (in KBr) are, on the whole, similar and have absorption bands ν(NH) (3384 cm$^{-1}$), ν(C=C), ν(C=N) (1618, 1575, and 1474 cm$^{-1}$), $\nu_{as}(NO_2)$ (1518 (**17a**) and 1532 cm$^{-1}$ (**17b**)), $\nu_s(NO_2)$ (1349 (**17a**) and 1346 cm$^{-1}$ (**17b**)), and ν(CH) (742 (**17a**) and 752 cm$^{-1}$ (**17b**)) characteristic of these structures. At the same time, a comparison of the spectra shows that the antisymmetric vibrations of the $NO_2$ group are most sensitive to structural changes (Table 3). Unlike the frequencies $\nu_s(NO_2)$, which are virtually identical in the spectra of both compounds, the frequency $\nu_{as}(NO_2)$ for compound **17b** is higher than that for **17a** by ~24 cm$^{-1}$. To exclude the influence of specific interactions, whose presence in the crystalline samples is evident from the low-frequency shifts of the NH absorption bands with ν(NH) = 3384 cm$^{-1}$ (in KBr) relative to free ν(NH) (3454 cm$^{-1}$), we recorded the IR spectra of solutions of compounds **17a** and **17b** in $CHCl_3$ (~$1 \cdot 10^{-2}$ mol L$^{-1}$) and $CCl_4$ (~$1 \cdot 10^{-3}$ mol L$^{-1}$). It was found that the above characteristic feature observed for the crystalline state is retained in solutions. In the spectra of solutions in $CHCl_3$, $\nu_{as}(NO_2)$ for compound **17b** (1546 cm$^{-1}$) is higher than that for compound **17a** (1533 cm$^{-1}$), in spite of the fact that the position of the ν(NH) band in solutions (at 3445 in $CHCl_3$ and 3452 cm$^{-1}$ in $CCl_4$) is indicative of the monomeric form of the molecules.

Therefore, the results of the present study demonstrate that hydrogen bonds are not responsible for the frequency effect ($\nu_{as}(NO_2)$) under consideration, and this effect can be related to different positions of the nitro group in the benzo fragment. It is known that the asymmetric vibrations of $NO_2$, which are sensitive to the electronic properties of the *para* substituent, are shifted to higher frequencies in the presence of electron-withdrawing substituents (1560—1540 cm$^{-1}$) or to lower frequencies (1550—1490 cm$^{-1}$) in the presence of electron-releasing substituents.[11,12] Taking into account that the benzoimidazole substituent at position 2 of the quinoxaline system has a specific π-deficient center, *viz.*, the μ-carbon atom, bearing a substantially higher positive charge[13] than that on the *ipso*-carbon atom of the Ph substituent at position 3, the frequency $\nu_{as}(NO_2)$ would be expected to be higher for isomer **17b** containing the nitro group at position 6 than that for isomer **17a**.

To confirm the structures of compounds **17a,b**, which were proposed based on the IR spectroscopic data, we synthesized acetyl derivative **18** of low-melting compound **17b** and prepared high-quality single crystals of this derivative.




**18**

**Table 3**. IR spectra of compounds **17a,b**

| Isomer | IR, ν/cm$^{-1}$ | | | | Conditions of measurement |
|---|---|---|---|---|---|
| | ν(NH, free) | ν(NH, bound) | $\nu_{as}(NO_2)$ | $\nu_s(NO_2)$ | |
| **17a** | — | 3384 | 1518 | 1350 | In KBr |
| **17a** | — | 3382 | 1518 | 1350 | In Nujol mulls |
| **17a** | 3452 | — | — | — | In $CCl_4$ |
| **17a** | 3445 | — | 1533 | 1348 | In $CHCl_3$ |
| **17b** | — | 3384 | 1532 | 1346 | In KBr |
| **17b** | — | 3386 | 1536 | 1345 | In Nujol mulls |
| **17b** | 3452 | — | — | — | In $CCl_4$ |
| **17b** | 3445 | — | 1546 | 1348 | In $CHCl_3$ |

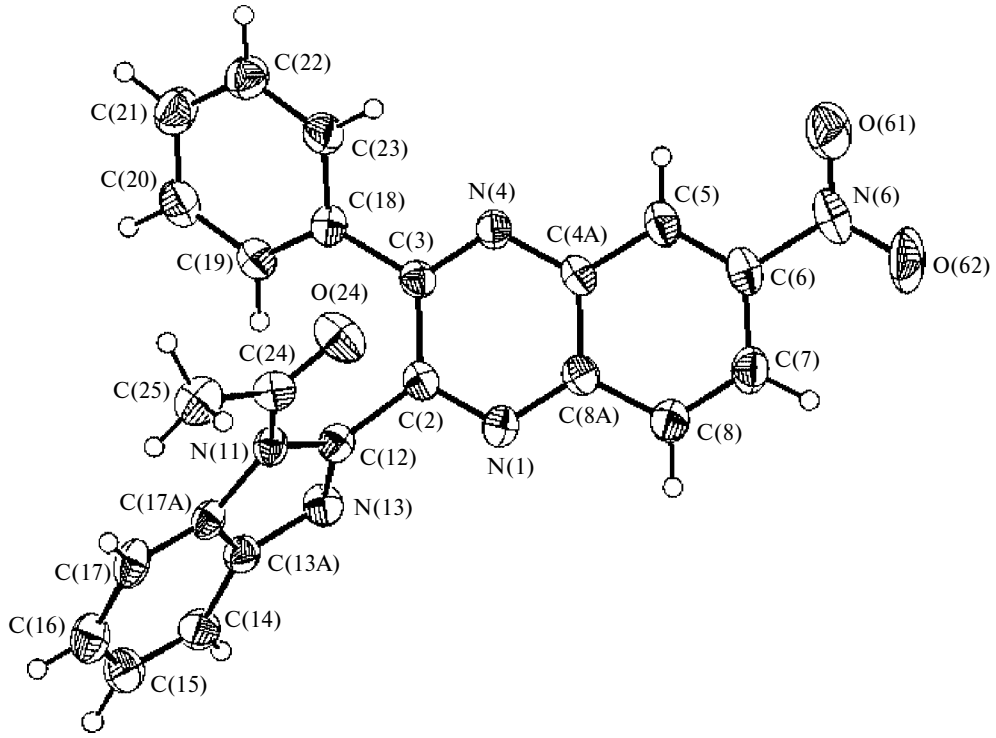



**Fig. 4.** Molecular structure of compound **18** in the crystal.

Compound **18** crystallized in the monoclinic space group $P2_1/c$ with one independent molecule per asymmetric unit (Fig. 4).

The conformation of molecule **18** is similar to that of compound **11** described above. The only difference is the angle of rotation of the Ph substituent and the benzoimidazole fragment with respect to the quinoxaline moiety.

However, in spite of similar conformations of these molecules, a redistribution of the bond lengths (significant within the experimental errors) is observed in the quinoxaline fragments (Table 4), which may be indicative of the different role of steric interactions in these molecules.

Interestingly, the nitro group in compound **18** lies virtually in the plane of the quinoxaline fragment (the O(62)—N(6)—C(6)—C(5) torsion angle is 176.8(4)°), which is favorable for the formation of intramolecular C—H...O contacts, *viz.*, C(7)—H(7)...O(62) and C(5)—H(5)...O(61) (O...H, 2.42(2) and 2.41(2) Å, respectively).

In the crystal of compound **18**, the molecules are involved in various intermolecular contacts. Analysis of these interactions revealed the phenomenon of supramolecular isomerism in the crystal consisting in the formation of various types of supramolecular structures depending on the type of contacts. For example, the intermolecular C—H...O contacts between the H(20) proton of the Ph substituent and the O(62′) atom of the nitro group (the symmetry operation $-x, -1/2 + y, 1/2 - z$; H...O, 2.56 Å; C—H...O, 146°) give rise to zigzag chains of hydrogen-bonded molecules along the crystallographic axis $0y$. In the crystal of the starting compound **11**, the H(253) proton of the Me group is involved in the intermolecular contact with the O(62″) atom of the nitro group of another molecule ($1 + x, 1/2 - y, 1/2 + z$; H...O, 2.51 Å; C—H...O, 130°), and the molecules are linked by these contacts in zigzag chains along the diagonal $x0z$. Finally, chains of hydrogen-bonded molecules along the crystallographic axis $0x$ are formed *via* the interactions between another proton of the Me group (H(252)) and the N(13′) atom of the adjacent molecule ($1 + x, y, z$; H...O, 2.74 Å; C—H...O, 116°).

In addition to the above-described intermolecular contacts, there are also numerous π—π interactions. In the crystal structure, the benzoquinoxaline fragments of all molecules are perpendicular to the crystallographic axis $0x$, the planes of the Ph rings slightly deviate from this axis, whereas the planes of the benzoimidazole fragments are coplanar to this axis. This arrangement of the molecules in the crystal is characterized by a rather high packing coefficient (69.5%). The involvement of the electron systems of the benzoquinoxaline fragments and the Ph rings in π—π interactions (the distances between the centers of the rings vary from 3.28 to 3.64 Å; the dihedral angles are in the range of 0—5.4°) gives rise to a three-dimensional supramolecular structure with pseudo-

**Table 4.** Selected geometric parameters of molecules **4**, **11**, and **18** (bond lengths (*d*), bond angles (ω), and torsion angles (τ))

| Parameter | **4** | **11** | **18** |
|---|---|---|---|
| Bond | | *d*/Å | |
| N(1)—C(2) | 1.323(2) | 1.313(4) | 1.301(4) |
| N(1)—C(8A) | 1.359(3) | 1.366(3) | 1.353(4) |
| N(4)—C(3) | 1.320(2) | 1.317(3) | 1.290(4) |
| N(4)—C(4A) | 1.366(2) | 1.357(4) | 1.382(4) |
| N(11)—C(12) | 1.363(2) | 1.359(3) | 1.394(4) |
| N(11)—C(17A) | 1.361(3) | 1.373(3) | 1.413(4) |
| N(13)—C(12) | 1.328(2) | 1.316(4) | 1.289(4) |
| N(13)—C(13A) | 1.388(2) | 1.387(3) | 1.401(4) |
| C(2)—C(3) | 1.439(2) | 1.440(4) | 1.459(4) |
| C(2)—C(12) | 1.463(3) | 1.484(3) | 1.492(5) |
| C(13a)—C(14) | 1.394(3) | 1.396(4) | 1.395(5) |
| C(13a)—C(17a) | 1.398(2) | 1.397(4) | 1.398(5) |
| C(4a)—C(8a) | 1.405(2) | 1.413(4) | 1.416(4) |
| Angle | | ω/deg | |
| C(2)—N(1)—C(8a) | 118.1(2) | 117.5(2) | 117.9(3) |
| C(3)—N(4)—C(4a) | 118.5(2) | 118.1(2) | 118.4(3) |
| C(12)—N(11)—C(17a) | 107.8(2) | 106.6(2) | 105.1(3) |
| C(12)—N(13)—C(13a) | 104.6(2) | 104.1(2) | 105.3(3) |
| C(3)—C(2)—C(12) | 125.7(2) | 121.9(2) | 124.3(3) |
| N(4)—C(3)—C(18) | 115.0(3) | 116.7(2) | 115.8(3) |
| N(11)—C(12)—C(2) | 119.7(2) | 123.0(2) | 124.4(3) |
| N(4)—C(4a)—C(8a) | 120.6(2) | 121.3(2) | 119.6(3) |
| C(2)—C(3)—C(18) | 124.5(2) | 122.9(2) | 123.3(3) |
| Angle | | τ/deg | |
| C(2)—N(1)—C(8a)—C(4a) | 2.1(4) | 2.5(4) | 1.7(5) |
| C(12)—N(13)—C(13a)—C(17a) | −0.5(2) | −0.6(3) | −1.5(3) |
| C(2)—C(3)—C(18)—C(23) | 150.2(2) | 134.0(3) | 149.4(3) |
| N(4)—C(4a)—C(8a)—N(1) | −7.4(3) | −1.0(5) | −4.2(5) |
| N(4)—C(3)—C(18)—C(23) | −35.5(3) | −45.8(4) | −32.3(4) |
| N(1)—C(2)—C(3)—N(4) | −9.9(3) | −1.0(4) | −5.4(5) |
| C(3)—C(2)—C(12)—N(11) | 163.2(5) | −66.8(3) | −70.8(4) |
| C(12)—C(2)—C(3)—C(18) | −19.2(3) | −1.1(4) | −3.7(5) |

channels parallel to the crystallographic axis 0*x* (Fig. 5). These channels are occupied by the benzoimidazole fragments of the molecules, and these fragments are involved in π—π interactions only in parallel with the corresponding centrosymmetrical pair (the distance between the centers of the rings is 3.48 Å; the dihedral angle is 0°). Presumably, the crystals of this compound possessing such a special direction should exhibit also substantial anisotropy of physical properties.

The reaction of benzoylquinoxalinone **1** with 3,4-diaminotoluene (**2c**), like that of nitro derivative **2b**, afforded a mixture of two isomers in virtually equal amounts, as evident from the $^1$H NMR spectra of this mixture. It should be noted that the reaction conditions have no noticeable influence on the ratio between the products. Unlike compounds **17a,b**, we failed to isolate these isomers and, hence, Tables 1 and 2 give the physicochemical and spectroscopic characteristics for a mixture of isomers. The composition of this mixture corresponds to a mixture of 2-(benzoimidazol-2-yl)-7-methyl-3-phenylquinoxaline (**19a**) and its 6-methyl isomer (**19b**).

Therefore, the quinoxaline-benzoimidazole rearrangement considered in the present study has a rather general character. If the first steps presented in Schemes 5 or 6 are rate-determining steps in the reactions giving rise to compounds **4** and **17a,b**, the reaction according to Scheme 5 would be expected to give predominantly compound **17a**, because this process corresponds to the faster reaction of the more nucleophilic amino group in the *meta* position with respect to the nitro group. Correspondingly, the reaction according to Scheme 6 should afford predominantly isomer **17b**. However, as mentioned above, isomers **17a,b** were produced in nearly equal amounts. Hence, either Schemes 5 and 6 are equally probable in the

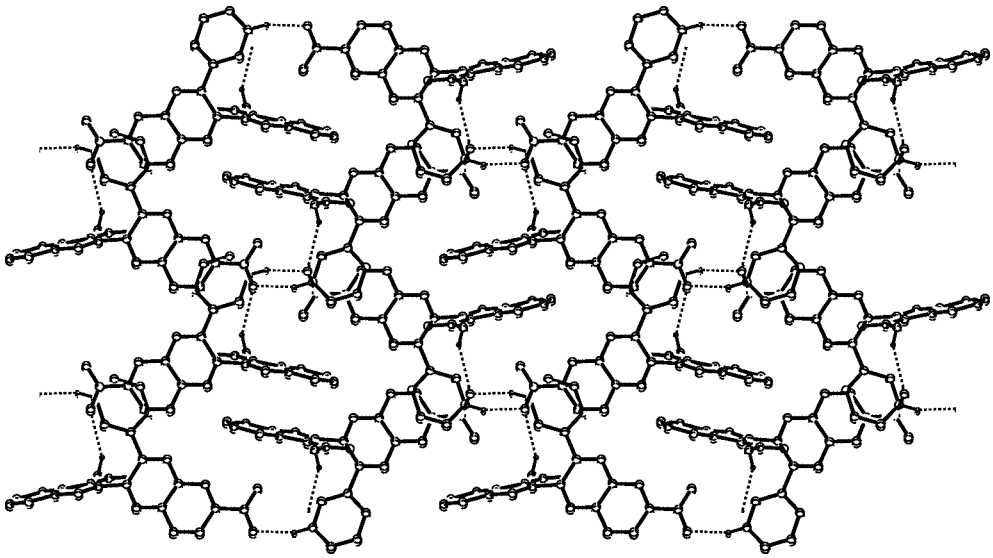


**Fig. 5.** Formation of pseudochannels in the crystal structure of compound **18** projected along the crystallographic axis 0*x*. Only H atoms involved in intermolecular contacts are shown.

course of the quinoxalinone-benzoimidazole rearrangement, or the first steps of these schemes are not rate-determining, or, alternatively, none of these schemes takes places.

## Experimental

The melting points were measured on a Boetius hot-stage apparatus. The IR spectra were recorded on a UR-20 spectrometer in Nujol mulls. The IR spectra of compounds **17a,b** were additionally measured on a Vector-22 (Bruker) Fourier-transform spectrometer in the following conditions: resolution was 1 $cm^{-1}$, 64 scans were accumulated, the scan time was 16 s. The $^1H$ NMR spectra were recorded on a Bruker-MCL-250 spectrometer (250.13 MHz) using signals of the corresponding solvent as the internal standard.

**1-Alkyl-3-benzoylquinoxalin-2-ones 5—10 (general procedure).** A mixture of compound **1** (4.0 mmol) and KOH (5.4 mmol) in dioxane (50 mL) was refluxed for 1 min. Then a solution of the corresponding alkyl halide (4.7 mmol) in dioxane (5 mL) was added. The reaction mixture was refluxed for 4 h and poured into water. The crystals that precipitated were filtered off, washed with a solution of KOH and water (~30 mL), dried in air, and recrystallized from the corresponding solvent. The physicochemical characteristics of compounds **5—10** are given in Tables 1 and 2.

**2-(1-Alkylbenzoimidazol-2-yl)-3-phenylquinoxalines 11—16 (general procedure).** A solution of the corresponding 1-alkyl-3-benzoylquinoxalin-2-one (0.95 mmol) and *o*-PDA (1.04 mmol) in AcOH (10 mL) was refluxed for 1 h, cooled, and poured into water. Then a solution of sodium carbonate was added. The crystals that precipitated were filtered off, washed with water (~30 mL), dried in air, and recrystallized from the corresponding solvent. The physicochemical characteristics of compounds **11—16** are given in Tables 1 and 2.

**2-(Benzoimidazol-2-yl)-7-nitro-3-phenyl- and -6-nitro-3-phenylquinoxalines (17a,b).** A solution of compound **1** (0.40 g, 1.60 mmol) and 4-nitro-1,2-phenylenediamine (0.28 g, 1.85 mmol) in AcOH (15 mL) was refluxed for 1 h. The crystals that precipitated were filtered off from the hot solution and washed with $Pr^iOH$ to isolate isomer **17a**. The solution in AcOH was poured into water. The crystals that precipitated were filtered off and isomer **17b** was isolated.

**2-(1-Acetylbenzoimidazol-2-yl)-6-nitro-3-phenylquinoxaline (18).** A solution of compound **17b** (50 mg, 0.14 mmol) in $Ac_2O$ (1 mL) was refluxed for 10 min, cooled, and poured into water. The crystals that precipitated were filtered off and washed with $Pr^iOH$.

**2-(Benzoimidazol-2-yl)-7-methyl-3-phenyl- and 6-methyl-3-phenylquinoxalines 19a,b.** A solution of compound **1** (0.40 g, 1.60 mmol) and 3,4-diaminotoluene (0.22 g, 1.8 mmol) in AcOH (5 mL) was refluxed for 1 h, cooled, and poured into water. Then a solution of sodium carbonate was added. The crystals that precipitated were filtered off and washed with water.

**X-ray diffraction study** was carried out on an automated four-circle Enraf-Nonius CAD-4 diffractometer. Crystals of **4**, $C_{21}N_4H_{15}$, are monoclinic, at 20 °C, $a$ = 8.181(3) Å, $b$ = 20.494(5) Å, $c$ = 10.364(4) Å, β = 112.77(3)°, $V$ = 1602.1(1) $Å^3$, $Z$ = 4, $d_{calc}$ = 1.34 g $cm^{-3}$, space group $P2_1/n$. Crystals of **11**, $C_{22}N_4H_{16}$, are triclinic, at 20 °C, $a$ = 6.389(1) Å, $b$ = 11.697(4) Å, $c$ = 12.621(6) Å, α = 71.19(4)°, β = 89.86(3)°, γ = 77.18(2)°, $V$ = 868.1(6) $Å^3$, $Z$ = 2, $d_{calc}$ = 1.29 g $cm^{-3}$, space group $P\bar{1}$. Crystals of **18**, $C_{23}N_5O_3H_{16}$, are monoclinic, at 20 °C, $a$ = 7.487(8) Å, $b$ = 21.28(2) Å, $c$ = 12.245(6) Å, β 102.07(5)°, $V$ = 1908(3) $Å^3$, $Z$ = 4, $d_{calc}$ = 1.43 g $cm^{-3}$, space group $P2_1/c$. The unit cell parameters and intensities of 3534 (for compound **4**), 2057 (for compound **11**), and 4194 (for compound **18**) reflections, of which 1874 (**4**), 1539 (**11**), and 2257 (**18**) reflections were with $I \geq 3\sigma$, were measured at 20 °C (λMo-Kα (**4** and **11**) and λCu-Kα radiation (**18**), graphite monochromator, ω/2θ scanning technique, θ ≤ 26.3° (**4** and **11**) and θ ≤ 74.2° (**18**)). The intensities of three check reflections showed no decrease in the course of X-ray data collection. Absorption was ignored (μ(Mo) = 0.76 (**4**), 0.73 $cm^{-1}$ (**11**), and μ(Cu) = 7.66 $cm^{-1}$ (**18**)). The structures were solved by direct methods using the SIR program[14] and refined first isotropically and then anisotropically. The H atoms were revealed from difference electron density syntheses. For **4**, the contributions of the H atoms to the structure amplitudes were refined in the final steps of the least-squares in the isotropic approximation. For **11** and **18**, the H atoms were included in the refinement with fixed positional and isotropic thermal parameters. The final reliability factors were as follows: $R$ = 0.040, $R_w$ = 0.044 based on 1874 independent reflections with $F^2 \geq 3\sigma$ (for **4**), $R$ = 0.042, $R_w$ = 0.122 based on 1472 independent reflections with $F^2 \geq 2\sigma$ (for **11**), and $R$ = 0.059, $R_w$ = 0.074 based on 1780 reflections with $F^2 \geq 3\sigma$ (for **18**). Calculations for the structure of **11** were carried out using the SHELXL-97 program package and the WinGX program on a personal computer. Calculations for the structures of **4** and **18** were performed using the MolEN program package[15] on an AlphaStation 200 computer. Selected geometric parameters of the all structures are given in Table 4. The molecular structures and molecular packings in the crystals were drawn and the intramolecular and intermolecular interactions were calculated with the use of the PLATON program.[16]

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## References

1. A. A. Kalinin, V. A. Mamedov, and Ya. A. Levin, *Khim. Geterotsikl. Soedin.*, 2000, 995 [*Chem. Heterocycl. Compd.*, 2000, **36** (Engl. Transl.)].
2. V. A. Mamedov, A. A. Kalinin, I. Kh. Rizvanov, N. M. Azancheev, Yu. Ya. Efremov, and Ya. A. Levin, *Khim. Geterotsikl. Soedin.*, 2002, 1279 [*Chem. Heterocycl. Compd.*, 2002, **38** (Engl. Transl.)].
3. V. A. Mamedov, A. A. Kalinin, A. T. Gubaidullin, I. A. Litvinov, and Ya. A. Levin, *Khim. Geterotsikl. Soedin.*, 2003, 101 [*Chem. Heterocycl. Compd.*, 2003, **39** (Engl. Transl.)].
4. V. A. Mamedov, A. A. Kalinin, A. T. Gubaidullin, I. Kh. Rizvanov, A. V. Chernova, G. M. Doroshkina, I. A. Litvinov,

and Ya. A. Levin, *Zh. Org. Khim.*, 2003, **39**, 141 [*Russ. J. Org. Chem.*, 2003, **39** (Engl. Transl.)].
5. P. Müller, *Pure Appl. Chem.*, 1994, **66**, 1077.
6. I. B. Dzvinchuk, *Khim. Geterotsikl. Soedin.*, 1999, 1687 [*Chem. Heterocycl. Compd.*, 1999, **35** (Engl. Transl.)].
7. L. A. Cescon and A. R. Day, *J. Org. Chem.*, 1962, **27**, 581.
8. M. B. Hogale and B. P. Nikam, *J. Ind. Chem. Soc.*, 1988, **LXV**, 735.
9. R. A. Ogg and F. W. Bergstrom, *J. Am. Chem. Soc.*, 1931, **53**, 1846.
10. E. C. Taylor and A. McKillop, *J. Org. Chem.*, 1965, **30**, 2858.
11. L. J. Bellamy, *Advances in Infrared Group Frequencies*, Methuen and Co. LTD, Bungay—Suffolk, 1968.
12. C. N. R. Rao, *Chemical Application of Infrared Spectroscopy*, Academic Press, New York—London, 1963, 272.
13. A. F. Pozharskii, *Teoreticheskie osnovy khimii geterotsiklov* [*Theoretical Fundamentals of Chemistry of Heterocycles*], Khimiya, Moscow, 1985, 236 pp. (in Russian).
14. A. Altomare, G. Cascarano, C. Giacovazzo, and D. Viterbo, *Acta Crystallogr., Sect. A*, 1991, **47**, 744.
15. L. H. Straver and A. J. Schierbeek, *MolEN. Structure Determination System, Vol. 1*, Program Description, Nonius B. V., 1994.
16. A. L. Spek, *PLATON. A Multipurpose Crystallographic Tool*, Utrecht University Press, Utrecht, 2000, 214 pp.

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