Dimerization of 3-(2-aryl-2-oxoethylidene)oxindoles

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6-Aroyl-7-arylindolo[3,4-*jk*]phenanthridin-5(4*H*)-ones (**2a**–**i**) were synthesized by heating 3-(2-aryl-2-oxoethylidene)-2,3-dihydroindol-2-ones (**1a**–**i**) in DMF. Compounds **2a**–**i** are formed *via* the dimerization of two molecules of unsaturated ketones **1a**–**i** proceeding as the [2+4] cycloaddition through the formation of intermediate spiro adducts. The further Pfitzinger rearrangement, decarboxylation, and heteroaromatization afford compounds **2a**–**i**. The structures of the reaction products were established by spectroscopic methods and X-ray diffraction.

Key words: oxindoles, dimerization, [2+4] cycloaddition, spiro adducts, indolophenanthridines.

3-(2-Aryl-2-oxoethylidene)oxindoles (3-(2-aryl-2-oxoethylidene)-2,3-dihydroindol-2-ones) are polyfunctional α ,β-unsaturated ketones having a wide range of reaction possibilities. The reactions with nucleophilic reagents,¹⁻³ the synthesis of 2-arylquinoline-4-carboxylic acids by the Pfitzinger reaction,⁴⁻⁶ and the [2+2],⁷ [2+3],⁸ and [2+4] cycloaddition reactions^{9,10} are of most importance.

In the present study, we investigated the dimerization of 3-(2-aryl-2-oxoethylidene)oxindoles **1a**—i under heating in a polar solvent (DMF).

Heating of 3-(2-methyl-2-oxoethylidene)oxindoles in toluene affords two dimers.^{11–13} 3,4-Diacetyl-1,2a,3,4tetrahydrospiro[benz[cd]indole-5,3'-indoline]-2(2H),2'dione was obtained as the major reaction product: 5-acetyl-2-(2,3-dihydro-2-oxo-1H-indol-3-yl)spiro-[cyclopentane-1,3'-(3H)indole]-2',3(1'H)-dione, as the minor product. The latter compound was identified by X-ray diffraction.¹³ Heating of 3-(2-aryl-2-oxoethylidene)oxindoles 1a-i in toluene or xylene did not yield any reaction products, and only the starting compounds were isolated from the solution. By contrast, heating of oxindoles 1 in DMF for 1 h gave compounds 2a-i in moderate yields. These compounds were identified by IR and ¹H NMR spectroscopy, mass spectrometry, and X-ray diffraction (for compound 2d) as 6-aroyl-7-arylindolo[3,4-jk]phenanthridin-5(4H)-ones (Scheme 1).

The IR spectra (Table 1) of compounds **2a**—i show the following characteristic bands: a low-intensity broad band at 3150 cm⁻¹ belonging to N—H stretching vibrations, two intense bands at 1690 and 1665 cm⁻¹ assigned to C=O stretching vibrations of the aroyl and oxindole carbonyl groups, respectively, and a medium-intensity band



 $\begin{array}{l} \mathsf{R} = \mathsf{H} \left(\textbf{a} - \textbf{f} \right), \mathsf{Br} \left(\textbf{g} \right), \mathsf{Me} \left(\textbf{h}, \textbf{i} \right); \mathsf{Ar} = \mathsf{Ph} \left(\textbf{a}, \textbf{h} \right), \mathsf{4}\text{-}\mathsf{ClC}_6\mathsf{H}_4 \left(\textbf{b} \right), \\ \mathsf{4}\text{-}\mathsf{BrC}_6\mathsf{H}_4 \left(\textbf{c}, \textbf{g}, \textbf{i} \right), \mathsf{4}\text{-}\mathsf{IC}_6\mathsf{H}_4 \left(\textbf{d} \right), \mathsf{4}\text{-}\mathsf{MeOC}_6\mathsf{H}_4 \left(\textbf{e} \right), 2\text{-naphthyl} \left(\textbf{f} \right) \end{array}$

at 1635 cm⁻¹ corresponding to a superposition of C=C and C=N stretching vibrations.

The ¹H NMR spectra of compounds 2a-f (Table 2) show a broad singlet for one proton, N(4)H, at δ 11, three doublets for the aromatic protons H(12), H(1), and H(9), with an integrated intensity of 1 H each, at δ 9.2, 8.8, and 8.2, respectively, and signals for H(12), H(1), and H(9)at δ 9.2, 8.8, and 8.2, respectively. The multiplet with an integrated intensity of 3 H at δ 7.8–8.0 corresponds to signals for H(2), H(10), and H(11). The signals for the aromatic protons H(3) of the aroyl substituent at position 6 and a part of the aromatic protons of the aryl substituent at position 7 of 6-aroyl-7-arylindolo[3,4-*ik*]phenanthridin-5(4*H*)-one are observed at δ 6.7–7.5 as a multiplet with an integrated intensity of 7 H–9 H. Compound 2f, which contains the naphthyl substituents and, correspondingly, bears a larger number of aromatic protons, is an exception. The signals at δ 6.1–7.2 can appear

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Table 1. IR spectra of compounds 2-4

$\begin{array}{c c c c c c c c c c c c c c c c c c c $	Com-		IR, v/cm ⁻¹	
2a 3152 $1692, 1665$ 163 2b 3163 $1697, 1663$ 163 2c 3158 $1693, 1661$ 163 2d 3159 $1698, 1657$ 164 2e 3172 $1688, 1665$ 163 2f 3162 $1693, 1667$ 163 2g 3167 $1699, 1665$ 163 2h 3169 $1692, 1668$ 163 2i 3161 $1690, 1662$ 163 4a- $1765, 1717, 1673$ 160 4b- $1760, 1721, 1667$ 159 4c- $1769, 1722, 1660$ 159 4e- $1769, 1722, 1660$ 159	pound	NH	C=0	C=C
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	2a	3152	1692, 1665	1632
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	2b	3163	1697, 1663	1637
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	2c	3158	1693, 1661	1635
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	2d	3159	1698, 1657	1641
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	2e	3172	1688, 1665	1639
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	2f	3162	1693, 1667	1637
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	2g	3167	1699, 1665	1632
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	2h	3169	1692, 1668	1637
$ \begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	2i	3161	1690, 1662	1639
	4 a	—	1765, 1717, 1673	1600
4c - 1762, 1728, 1660 160 4d - 1769, 1722, 1660 159 4e - 1769, 1722, 1660 159	4b	—	1760, 1721, 1667	1598
4d – 1769, 1722, 1660 159 4e – 1769, 1722, 1660 159	4c	_	1762, 1728, 1660	1602
4e – 1769, 1722, 1660 159	4d	_	1769, 1722, 1660	1599
	4 e	—	1769, 1722, 1660	1599

either as a broad singlet with an integrated intensity of 2 H or as two broad singlets with an integrated intensity of 1 H each. The addition of deuteromethanol to the sample under study led to the disappearance of the signal for one

Table 2. ¹H NMR spectra of compounds $2a-i(\delta, J/Hz)$

proton at δ 11. This fact and the chemical shift of this signal characteristic of NH of oxindole systems provide evidence that compounds 2a-f contain only one oxindole fragment. The integrated intensity of the broad singlets at δ 6.1–7.2 remains virtually unchanged upon the addition of deuteromethanol and, consequently, these singlets cannot be assigned to mobile protons giving this type of signals. At the same time, an increase in the temperature led to changes in the character of these signals. At 30 °C, the signals appear as broadened singlets; at 60 °C, the signals coalesce; at 90 °C, the signals appear as a slightly broadened singlet with an integrated intensity of 2 H at δ 7. This dependence is characteristic of systems with the hindered rotation of aryl substituents about a single bond.¹⁴ The unexpectedly large chemical shifts of the doublets for the protons H(12) and H(1)(9.2 and 8.8 ppm, respectively) and the retention of the characteristic aromatic spin-spin coupling constant (8.2 Hz) suggest that the protons can be influenced by diamagnetic ring currents of more than one benzene ring. It should be noted that the introduction of 5-substituted 3-(2-aryl-2-oxoethylidene)-1,3-dihydroindol-2-ones **1g**—i into the reaction leads to changes in the spectral pattern of this portion of the ¹H NMR spectra of com-

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Com- pound	Aromatic protons	NH (s, 1 H)	Other protons
2a	9.21 (d, 1 H, H(12), <i>J</i> = 7.9); 8.74 (d, 1 H, H(1), <i>J</i> = 8.5);	11.06	_
	8.31 (d, 1 H, H(9), J = 7.9); 7.83 - 8.05 (m, 3 H, H(2), H(10), H(11));		
	7.08-7.57 (m, 9 H, H(3), Ar); 6.81, 6.51 (both br.s, 1 H each, Ar)		
2b	9.27 (d, 1 H, H(12), $J = 7.9$); 8.72 (d, 1 H, H(1), $J = 8.5$);	11.08	—
	8.22 (d, 1 H, H(9), J = 7.9); 7.83 - 8.05 (m, 3 H, H(2), H(10), H(11));		
	7.27 - 7.55 (m, 7 H, H(3), Ar); 6.86, 6.54 (both br.s, 1 H each, Ar)		
2c	9.24 (d, 1 H, H(12), $J = 7.9$); 8.73 (d, 1 H, H(1), $J = 8.5$);	10.86	—
	8.20 (d, 1 H, H(9), J = 7.9); 7.81 - 8.01 (m, 3 H, H(2), H(10), H(11));		
	7.22–7.56 (m, 7 H, H(3), Ar); 7.20, 6.91 (both br.s, 1 H each, Ar)		
2d	9.25 (d, 1 H, H(12), $J = 7.9$); 8.74 (d, 1 H, H(1), $J = 8.5$);		
	8.20 (d, 1 H, H(9), J = 7.9); 7.80 - 8.01 (m, 3 H, H(2), H(10), H(11));	10.92	—
	7.26–7.59 (m, 7 H, H(3), Ar); 7.19, 6.88 (both br.s, 1 H each, Ar)		
2e	9.23 (d, 1 H, H(12), $J = 7.9$); 8.70 (d, 1 H, H(1), $J = 8.5$);	10.85	3.80, 3.63
	8.17 (d, 1 H, H(9), J = 7.9); 7.81 - 7.99 (m, 3 H, H(2), H(10), H(11));		(both s, 3 H each, OMe)
	6.74–7.43 (m, 7 H, H(3), Ar); 7.51, 6.13 (both br.s, 1 H each, Ar)		
2f	9.30 (d, 1 H, H(12), J = 7.9); 8.79 (d, 1 H, H(1), J = 8.5);	10.92	—
	8.21 (d, 1 H, H(9), J = 7.9); 7.24–8.18 (m, 17 H, H(3), Ar);		
	7.03, 6.59 (both br.s, 1 H each, Ar)		
2g	8.11 (d, 1 H, H(9), J = 8.6); 8.02 (s, 1 H, H(12)); 7.80–7.86	10.97	_
	(m, 2 H, H(2), H(10)); 7.21–7.59 (m, 7 H, H(3), Ar);		
	7.11, 6.78 (both br.s, 1 H each, Ar)		
2h	8.06 (d, 1 H, H(9), J = 8.5); 7.96 (s, 1 H, H(12));	10.81	2.62, 2.58
	7.67–7.76 (m, 2 H, H(2), H(10)); 7.23–7.56 (m, 9 H, H(3), Ar);		(both s, 3 H each, Me)
	6.99, 6.74 (both br.s, 1 H each, Ar)		
2i	8.12 (d, 1 H, H(9), J = 8.5); 8.00 (s, 1 H, H(12)); 7.69–7.77	10.83	2.62, 2.57
	(m, 2 H, H(2), H(10)); 7.22–7.50 (m, 7 H, H(3), Ar);		(both s, 3 H each, Me)
	7.12, 6.79 (both br.s, 1 H each, Ar)		· · · · · · · · · · · · · · · · · · ·

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pounds **2g**—i. Thus, the doublet at δ 8.8 corresponding to H(1) disappears, the integrated intensity of the multiplet at δ 8.0—7.8 decreases to two protons due to the disappearance of the signal for H(11), and the doublet for H(12) at δ 9.2 appears at higher field as a singlet with a chemical shift of 8 ppm, which can indicate that the system becomes nonplanar due to the steric mutual influence of the substituents at positions 1 and 11 of 6-aroyl-7-arylindolo[3,4-*jk*]phenanthridin-5(4*H*)-one.

The mass spectra of compounds 2a-i (Table 3) have molecular ion peaks of 6-aroyl-7-arylindolo[3,4-*jk*]-phenanthridin-5-(4*H*)-ones corresponding to the molecular weights of these compounds.

The structures of compounds **2** were conclusively established by X-ray diffraction study of 6-(4-iodobenzoyl)-7-(4-iodophenyl)indolo[3,4-*jk*]phenanthridin-5(4*H*)-one (**2d**) (Fig. 1, Table 4).

The polycyclic fragment in molecule **2d** is nonplanar. Due to the rather strong repulsion between the substituents at the C(12) and C(11) atoms (the shortened intramolecular C(19)...C(26) contact is 2.83 Å; the sum of the van der Waals radii is 3.42 Å)¹⁵ and the repulsions between the atoms of the aromatic rings C(1)–C(4)...C(8) and C(13)...C(18) (the shortened intramolecular contacts are H(14)...C(7), 2.52 Å (2.87 Å); H(7)...C(14), 2.63 Å (2.87 Å); H(7)...H(14), 1.91 Å (2.34 Å)), the pyridine and benzene rings C(2)–C(1)–C(8)...C(11) are substantially nonplanar. The endocyclic torsion angles are as large as 14.5°.

The angle between the planes of the terminal benzene rings is 20.6° . The steric factors (the shortened intramolecular contacts are C(19)...C(27), 3.22 Å; C(19)...C(31), 3.31 Å; C(20)...C(26), 3.30 Å; C(20)...C(31), 3.23 Å; C(25)...C(31), 3.15 Å; the sum of the van der Waals radii is 3.42 Å) are responsible also for a substantial twist of the iodophenyl and iodobenzoyl sub-

Table 3.	Mass-spectrometric	data for compounds	2a-i (EI, 70 eV)
	1	F F F F F F F F F F F F F F F F F F F	

stituents with respect to the tetracyclic fragment (the C(10) - C(11) - C(19) - O(2)and N(2)-C(12)-C(26)-C(27) torsion angles are $-70.8(8)^{\circ}$ and $-71.5(7)^{\circ}$, respectively). This is accompanied by an increase in the C(10)-C(11)-C(19) and C(10) - C(12) - C(26)bond angles $(123.3(5)^{\circ})$ and 121.2(4)°, respectively) compared to the C(2)-C(11)-C(19) and N(2)-C(12)-C(26) bond angles (118.7(5)° and 114.8(5)°, respectively) and an elongation of the C(11)-C(19) and C(12)-C(26) bonds to 1.516(8) and 1.512(8) Å, respectively (the average bond length is 1.478 Å).¹⁵ In addition, the following bonds are elongated: C(17)-C(18), 1.435(7) Å; C(9)-C(13), 1.454(7) Å; C(9)-C(10), 1.420(7) Å; C(8)-C(9), 1.443(8) Å; C(7)-C(8), 1.440(8) Å; C(5)-C(6), 1.428(8) Å; C(10)-C(11), 1.454(7) Å; and C(10)-C(12), 1.452(8) Å. The C(16)-C(17), C(2)-C(11), and C(6)-C(7) bonds are shortened (1.339(9), 1.320(8), and 1.342(8) Å, respectively) compared to the standard length of the aromatic carbon-carbon bonds (1.384 Å). However, these bondlength deformations and, consequently, the deviation from aromaticity are typical of polycyclic systems.¹⁶

In the crystal structure, the molecules are packed in stacks along the twofold screw axis due to stacking interactions between the polycyclic fragments of the reference molecule and the symmetry-related molecule (0.5 - x, -0.5 + y, -0.5 - z). The mean planes of the rings are strictly parallel. The distance between the rings is 3.451(2) Å. The stacks are linked to each other by the intermolecular N(1)-H(1N)...O(1)' hydrogen bonds (-x, 1 - y, -z) (H...O, 2.04 Å; N-H...O, 158°) and the strongly shortened I(2)...I(1)' contacts (0.5 - x, 0.5 + y, 0.5 - z) with a length of 3.69 Å (4.30 Å). Apparently, the formation of the latter contacts leads to the deviation of the I(2) atom from the mean plane of the parent ben-

Com- pound	$m/z (I_{\rm rel} (\%))^*$
2a	450 $[M]^+$ (8), 373 $[M - C_6H_5]^+$ (5), 345 $[M - C_6H_4CO]^+$ (57), 105 $[C_6H_4CO]^+$ (100)
2b	518 [M] ⁺ (11), 407 [M - 4-Cl-C ₆ H ₄] ⁺ (4), 379 [M - 4-Cl-C ₆ H ₄ CO] ⁺ (62), 139 [C ₆ H ₄ CO] ⁺ (100)
2c	
2d	702 $[M]^+$ (7), 499 $[M - 4 - I - C_6 H_4]^+$ (52), 471 $[M - 4 - I - C_6 H_4 CO]^+$ (9), 344 $[M - 4 - I - C_6 H_4 CO - I]^+$ (13), 231 $[4 - I - C_6 H_4 CO]^+$ (100)
2e	$510 [M]^{+} (12), 403 [M - 4 - CH_{3}O - C_{6}H_{4}]^{+} (4), 375 [M - 4 - CH_{3}O - C_{6}H_{4}CO]^{+} (62), 135 [4 - CH_{3}O - C_{6}H_{4}CO]^{+} (100)$
2f	550 [M] ⁺ (4), 423 [M – naphthyl] ⁺] ⁺ (6), 395 M – naphthoyl] ⁺ (32), 155 [naphthoyl] ⁺ (100)
2g	766 $[M]^+$ (4), 607 $[M - 4 - Br - C_6 H_4]^+$ (21), 582 $[M - 4 - Br - C_6 H_4 CO]^+$ (30), 502 $[M - 4 - Br - C_6 H_4 CO - Br]^+$ (100), 184 $[4 - Br - C_6 H_4 CO]^+$ (92)
2h	478 $[M]^+$ (7), 401 $[M - C_6H_4]^+$ (8), 373 $[M - C_6H_4CO]^+$ (42), 105 $[C_6H_4CO]^+$ (100)
2i	636 $[M]^+$ (4), 480 $[M - 4 - Br - C_6H_4]^+$ (11), 452 $[M - 4 - Br - C_6H_4CO]^+$ (23), 373 $[M - 4 - Br - C_6H_4CO - Br]^+$ (100), 184 $[4 - Br - C_6H_4CO]^+$ (67)

* In addition, the plasma-desorption mass spectra (PDMS) were measured for compounds 2e and 2f, m/z: 511 [M + H]⁺ (2e), 551 [M + H]⁺ (2f).



Fig. 1. Molecular structure of compound 2d.

zene ring by 0.16 Å. The iodophenyl fragments linked by the I...I contact are in a T-shaped orientation relative to each other, due to which no substantial deviations from planarity are observed for the iodobenzoyl substituent (the rms deviation of the atoms from the plane is 0.017 Å).

Evidently, the molecules of compounds 2 consist of the 3-(2-aryl-2-oxoethylidene)oxindole and 2-arylquinoline fragments. Therefore, two pathways giving rise to the indolophenanthridine molecule can be suggested. One pathway involves the Pfitzinger rearrangement of one molecule of 3-(2-aryl-2-oxoethylidene)oxindole 1 into 2-arylquinoline-4-carboxylic acid followed by the reaction with the second 3-(2-aryl-2-oxoethylidene)oxindole molecule. Another pathway involves the Diels—Alder reaction of two molecules of 3-(2-aryl-2-oxoethylidene)oxindole **1**, one double bond of the diene component being involved in the aromatic system of the molecule.

Upon heating of 3-(2-aryl-2-oxoethylidene)oxindole **1a** with 2-arylquinoline-4-carboxylic acids (or 2-arylquinolines) in DMF, indolophenanthridine containing the benzoyl substituent corresponding to 3-(2-aryl-2oxoethylidene)oxindole **1a** at position 6 and the aryl substituent corresponding to 2-arylquinoline-4-carboxylic acid (or 2-arylquinoline) at position 7 was not detected.

Table 4. Selected bond lengths and bond angles in molecule

Bond	d∕Å	Bond	$d/\text{\AA}$	Angle	ω/deg	Angle	ω/deg
I(1)-C(23)	2.118(7)	I(2)—C(29)	2.097(7)	C(3) - N(1) - C(4)	112.7(4)	C(11)—C(2)—C(1)	121.9(5)
O(1) - C(3)	1.216(7)	O(2) - C(19)	1.216(8)	C(8) - C(1) - C(4)	125.4(5)	C(1) - C(2) - C(3)	104.8(5)
N(1) - C(3)	1.349(8)	N(2) - C(4)	1.399(7)	C(4) - C(1) - C(2)	110.5(5)	O(1) - C(3) - C(2)	127.2(5)
N(2)-C(12)	1.319(7)	N(2)-C(18)	1.367(7)	C(11) - C(2) - C(3)	133.3(5)	C(5) - C(4) - C(1)	120.3(5)
C(1)–C(8)	1.391(7)	C(1) - C(4)	1.393(7)	O(1) - C(3) - N(1)	127.5(5)	C(1) - C(4) - N(1)	106.4(5)
C(1) - C(2)	1.404(8)	C(2)–C(11)	1.320(8)	N(1) - C(3) - C(2)	105.3(5)	C(7) - C(6) - C(5)	124.6(6)
C(2) - C(3)	1.517(7)	C(4) - C(5)	1.358(9)	C(5) - C(4) - N(1)	133.2(5)	C(1) - C(8) - C(7)	113.3(5)
C(5) - C(6)	1.428(8)	C(6) - C(7)	1.342(8)	C(4) - C(5) - C(6)	115.6(5)	C(7) - C(8) - C(9)	130.9(5)
C(7) - C(8)	1.440(8)	C(8) - C(9)	1.443(8)	C(6) - C(7) - C(8)	120.6(5)	C(2) - C(11) - C(19)	118.7(5)
C(9)-C(10)	1.420(7)	C(9) - C(13)	1.454(7)	C(1) - C(8) - C(9)	115.4(5)	N(2) - C(12) - C(10)	123.6(5)
C(10)-C(12)	1.452(8)	C(10)-C(11)	1.454(7)	C(10) - C(11) - C(19)	123.3(5)	N(2)-C(18)-C(13)	125.3(4)
C(11)–C(19)	1.516(8)	C(12)-C(26)	1.512(8)	N(2) - C(12) - C(26)	114.8(5)	O(2)-C(19)-C(11)	116.9(6)
C(13)-C(18)	1.386(8)	C(13)-C(14)	1.405(8)	N(2)-C(18)-C(17)	115.3(5)		
C(14)-C(15)	1.378(8)	C(15)-C(16)	1.36(1)	O(2)-C(19)-C(20)	124.2(6)		
C(16)-C(17)	1.339(9)	C(17)-C(18)	1.435(7)	C(12) - N(2) - C(18)	116.8(5)		
C(19)-C(20)	1.465(9)	C(20)-C(25)	1.372(9)	C(8) - C(1) - C(2)	124.1(5)		

Compound **2a** was the only indolophenanthridine isolated from the reaction mixture. The yield of compound **2a** based on 3-(2-aryl-2-oxoethylidene)oxindole **1a** differs only slightly from that obtained according to the standard procedure without the use of 2-arylquinoline-4carboxylic acid (or 2-arylquinoline). Based on this fact, the first pathway giving rise to the indolophenanthridine system can be excluded (Scheme 2).

Scheme 2



The dimerization of compounds **1** in acetic anhydride unambiguously demonstrated that this reaction proceeds as the [2+4]-cycloaddition, one 3-(2-aryl-2-oxoethylidene)-2,3-dihydroindol-2-one molecule (**1**) acting asthe diene and another molecule serving as a dienophile.This reaction involves the following successive one-potprocesses: the introduction of the acyl protecting groupinto the NH centers of the oxindole bicyclic systems ofstarting <math>3-(2-aryl-2-oxoethylidene)oxindoles **1**, which allows the exclusion of the Pfitzinger rearrangement, and the dimerization of the resulting *N*-acetyl-3-(2-aryl-2-oxoethylidene)oxindoles **3** (Scheme 3).

The reaction affords 1,1'-diacetyl-3,4-diaroyl-1,2,2a,3,4,5-hexahydrospiro[benz[*cd*]indol-5,3'-indoline]-2,2'(1'*H*)-diones **4a**—**e**, which were identified by IR and ¹H NMR spectroscopy and the X-ray diffraction study of compound **4a**. The IR spectra of **4a**—**e** recorded in KBr pellets show characteristic intense bands at 1765, 1700, and 1675 cm⁻¹ corresponding to stretching vibrations of the aroyl, acetyl, and oxindole carbonyl groups and a medium-intensity band at 1600 cm⁻¹ corresponding to a superposition of stretching vibrations of the aromatic C=C bonds.

The ¹H NMR spectra of compounds 4a-e (Table 5) show two singlets for the methyl protons of the acetyl fragments of the spiroacenaphthylenone molecule at δ 2.22–2.45. The signals of the AMX system for the protons of the cyclohexene fragment appear as a doublet with an integrated intensity of 1 H at δ 4.33–4.45 (the signal for the proton at the bridgehead C(2a) atom) and a multiplet with an integrated intensity of 2 H at δ 4.77–5.05 (the signals for the protons at positions 3 and 4 of the benzindole fragment). The signals for the protons of the aromatic moieties of compounds 4a-e are observed at δ 6.85–7.41. The doublet for one aromatic proton is substantially shifted upfield (δ 6.33–6.44) and corresponds to the signal for the ortho proton of the aroyl substituent at position 4 of the benzindole system. The upfield shift of the signal is associated with the fact that this proton is located above the plane of the benzene ring of the 3-spirooxindole fragment of molecule 4.

The structures of compounds 4a - e were conclusively established by the X-ray diffraction study of 1,1'-diacetyl-3,4-dibenzoyl-1,2,2a,3,4,5-hexahydrospiro[benz-[*cd*]indol-5,3'-indoline]-2,2'(1*H*)dione 4a (Fig. 2, Tables 6 and 7).



Fig. 2. Molecular structure of compound 4a.



3, **4**: Ar = Ph (**a**), 4-ClC₆H₄ (**b**), 4-BrC₆H₄ (**c**), 4-MeOC₆H₄ (**d**), 2-thienyl (**e**)

The tetrahydro ring involved in the tricyclic fragment adopts a sofa conformation (the puckering parameters¹⁷ are S = 0.82, θ = 41.2°, ψ = 0.9°). The deviation of the C(8) atom from the mean plane passing through the other atoms of the ring is 0.77 Å. The bicyclic fragment spirofused to the tetrahydro ring is planar within 0.02 Å and is located virtually perpendicular to the plane of the tricyclic fragment (the C(10)-C(5)-C(6)-C(28) torsion angle is $116.3(2)^{\circ}$). This gives rise to the shortened intramolecular H(4)...C(34) contact (2.78 Å; the sum of the van der Waals radii is 2.87 Å). The acyl substituent at the N(2) atom is noncoplanar with the plane of the bicyclic fragment (the C(28)-N(2)-C(35)-C(36) torsion angle is $7.9(3)^{\circ}$), which is apparently attributed to the presence of the shortened intramolecular contacts: H(30)...O(4), 2.23 Å (2.46 Å); H(30)...C(35), 2.84 Å (2.87 Å); H(36b)...O(3), 2.40 Å (2.46 Å); H(36b)...C(28), 2.82 Å (2.87 Å).

The benzoyl substituent at the C(7) atom is in an equatorial orientation with respect to the mean plane of the tetrahydro ring (the C(5)–C(6)–C(7)–C(21) torsion angle is $-157.0(1)^{\circ}$), resulting in the formation of the shortened intramolecular H(7)...H(9) contact with a length of 2.30 Å (2.34 Å). This substituent is oriented in such a way that the benzene ring adopts an *sc* conformation with respect to the C(6)–C(7)–C(21) torsion angle is $-70.3(2)^{\circ}$).

Strong repulsions between the atoms of the tetrahydro ring and the atoms of the aromatic ring C(22)...C(27) (shortened intramolecular contacts: H(7)...C(23), 2.67 Å (2.87 Å); H(7)...H(23), 2.19 Å (2.34 Å); H(23)...C(7), 2.84 Å (2.87 Å)) are responsible for the twist of the benzene ring with respect to the C(7)–C(21) bond (the C(7)–C(21)–C(22)–C(27) torsion angle is 134.7(2)°). The bicyclic fragment and the aromatic ring of the benzoyl substituent at the C(7) atom are virtually parallel to each other; the distance between these moieties is 3.3–3.6 Å, which suggests the presence of intramolecular stacking interactions. Two rather bulky substituents at the adjacent carbon atoms in the tetrahydro ring cause also a substantial elongation of the C(6)–C(7) bond to 1.577(2) Å compared to its average value (1.540 Å).

The benzoyl substituent at the C(8) atom is in an equatorial orientation (the C(14)—C(8)—C(19)—C(10) torsion angle is 179.2(1)°). The benzene ring is virtually perpendicular to the plane of the tetrahydro ring and is twisted with respect to the C(8)—C(14) bond (the C(9)—C(8)—C(14)—C(15) and C(8)—C(14)—C(15)—C(16) torsion angles are $-89.7(2)^{\circ}$ and $157.1(2)^{\circ}$, respectively) due, apparently, to repulsions between the atoms of the tetrahydro ring and the aromatic ring (shortened intramolecular contacts: H(8)...C(20), 2.61 Å (2.87 Å); H(8)...H(20), 2.02 Å (2.34 Å); H(20)...C(8), 2.67 Å (2.87 Å)).

Com-	CH ₃	CH ₃	AMX system	Aromatic protons	Other
pound	(S, 5 H,	<u>Me</u> CO)			protons
4 a	2.25	2.46	4.44 (d, 1 H, H(5a),	6.37 (d, 1 H, H(2) of 6-aroyl, $J = 8.5$);	_
			J = 10.5; 4.97—5.07	7.10 (d, 2 H, Ar, J = 7.8); 7.16–7.21	
			(m, 2 H, H(6), H(7))	(m, 2 H, Ar); 7.27–7.37, 7.51–7.55	
				(both m, 4 H each, Ar); 7.66 (t, 1 H, Ar,	
				J = 7.8; 7.82, 7.87 (both d, 1 H each,	
				Ar, $J = 7.8$; 8.24 (d, 2 H, Ar, $J = 8.5$)	
4b	2.23	2.44	4.42 (d, 1 H, H(5a),	6.43 (d, 1 H, H(2) of 6-arovl, $J = 8.5$);	_
			J = 10.6; 4.99–5.10	7.21 (d, 2 H, Ar, $J = 8.2$); 7.27–7.35	
			(m, 2 H, H(6), H(7))	(m, 2 H, Ar); 7.41–7.47 (m, 4 H, Ar);	
				7.54–7.59 (m, 2 H, Ar): 7.70 (t, 1 H,	
				Ar. $J = 8.5$); 7.87, 7.92 (both d. 1 H each.	
				Ar. $J = 7.8$; 8.25 (d. 2 H. Ar. $J = 8.5$)	
4c	2.23	2.47	4.43 (d. 1 H. H(5a).	6.39 (d, 1 H, H(2) of 6-arovl, $J = 8.5$):	_
			J = 10.5; 4.98-5.11	7.18 (d, 2 H, Ar, $J = 8.2$): 7.24–7.31	
			(m, 2, H, H(6), H(7))	(m, 2 H, Ar); 7.37–7.43 (m, 4 H, Ar);	
			(,,(-),(-))	$7.58 - 7.62 \text{ (m } 2 \text{ H } \text{ Ar}) \cdot 7.67 \text{ (t } 1 \text{ H}$	
				Ar $J = 8$ 3): 7 84 7 89 (d 1 H Ar	
				J = 7.8): 8.25 (d. 2 H Ar $J = 8.5$)	
4d	2.30	2.45	4.32 (d. 1 H. H(5a).	6.35 (d, 1 H, H(2) of 6-aroyl, $J = 8.0$):	3.75. 3.85
	2100	2110	J = 10.2 · 4.83—4.96	$6.88 (d 2 H Ar J = 8.2) \cdot 7.01 (d 2 H$	(both s
			(m 2 H H(6) H(7))	Ar $J = 8.4$): 7.11-7.29 (m 6 H Ar):	3 H each
			(11, 2 11, 11(0), 11(7))	7 80-7 86 (m 3 H Ar): 8 17 (d 2 H	OMe)
				Ar $J=8.7$)	01110)
40	2 40	2 47	441 (d 1 H H(5a)	6.42 (d 1 H H(2) of 6-thienovl $I = 7.6$):	_
-10	2.10	2.17	I = 10.2 · · 4.76 - 4.83	$7.16-7.30 \text{ (m } 6 \text{ H } \text{ Ar}) \cdot 7.65 \text{ (d } 1 \text{ H}$	
			(m 2 H H(6) H(7))	Ar $I = 6.2$): 7.85–7.93 (m. 4 H. Ar):	
			(m, 2 m, 10), m(7)	8 02 8 37 (d 1 H Ar I = 6 2)	
				(0.02, 0.57, (0, 111, 71, 5 - 0.2))	

Table 5. ¹H NMR spectra of compounds **4a**–**e** (δ , *J*/Hz)

The five-membered heterocycle involved in the tricyclic fragment adopts an envelope conformation. The deviation of the C(11) atom from the mean plane passing through the other atoms of the ring is 0.18 Å. The acyl substituent at the N(1) atom is slightly twisted with respect to the N(1)-C(1) bond (the C(1)-N(1)-C(12)-O(2) torsion angle is $-10.1(2)^\circ$), which is, apparently, attrib-

Table 6. Selected bond lengths in molecule 4a

Bond	$d/\text{\AA}$	Bond	$d/{ m \AA}$
N(1)—C(12)	1.396(2)	N(2)—C(28)	1.396(2)
N(1) - C(1)	1.430(2)	N(2) - C(29)	1.421(2)
N(2)-C(35)	1.409(2)	O(2) - C(12)	1.204(2)
O(1) - C(11)	1.194(2)	O(4) - C(35)	1.193(2)
O(3)-C(28)	1.196(2)	O(6)-C(14)	1.205(2)
O(5)-C(21)	1.204(2)	C(1) - C(10)	1.387(2)
C(1) - C(2)	1.361(2)	C(5) - C(10)	1.366(2)
C(5) - C(6)	1.517(2)	C(6) - C(34)	1.500(2)
C(6)-C(28)	1.523(2)	C(6) - C(7)	1.577(2)
C(7) - C(21)	1.507(2)	C(7) - C(8)	1.525(2)
C(8) - C(14)	1.515(2)	C(8) - C(9)	1.526(2)
C(9)-C(10)	1.474(2)	C(9)-C(11)	1.508(2)
C(12)-C(13)	1.485(3)	C(14) - C(15)	1.474(2)
N(1)-C(11)	1.417(2)		

uted to the presence of the attractive H(2)...O(2) interaction with a length of 2.33 Å (2.46 Å).

The X-ray diffraction data and the absence of doubling of the same-type signals in the ¹H NMR spectra of compounds 4a-e provide evidence that the dimerization of *N*-acetyl-3-(2-aryl-2-oxoethylidene)oxindoles affords the only diastereomer, which is an important argument that this reaction proceeds as the [2+4] cycloaddition.

The removal of the acetyl groups from compound 4a gave rise to *N*-unsubstituted spiro[benzindole-5,3'-indoline]dione 5. Heating of the latter in DMF afforded 6-benzoyl-7-phenylindolo[3,4-*jk*]phenanthridin-5-(4*H*)-one (**2a**). This compound is identical to the product synthesized under the same conditions from 3-(2-oxo-2phenylethylidene)oxindole **1a**.

Therefore, the dimerization of 3-(2-aryl-2-oxo-ethylidene)oxindoles 1a-i, like that of *N*-acetyl-3-(2-aryl-2-oxoethylidene)oxindoles 3a-e, proceeds as the Diels—Alder reaction with the involvement of dienes (see Scheme 3). The aromaticity of the benzene ring in the tricyclic fragment of the intermediate molecule is recovered as a result of the 1,3-hydrogen shift giving rise to spirobenzindoleindolines 5a-e. Compounds 5a-e

Table 7. Bond angles in molecule 4a

undergo the Pfitzinger rearrangement (Scheme 3). The subsequent decarboxylation and heteroaromatization

under severe reaction conditions afford indolophenanthridine systems 2a—i.

Table 8. Yields and physicochemical characteristics of compounds 2a-i and 4a-e

Com- дине-	Yield (%)	Yield M.p. (%) /°C	<u>]</u> (Found Calculated	Molecular formula	
			С	Н	N	
2a	62	374-376	82.31	<u>3.99</u>	<u>6.24</u>	$C_{31}H_{18}N_2O_2$
			82.65	4.03	6.22	
2b	60	375-377	<u>71.73</u>	<u>3.08</u>	<u>5.36</u>	$C_{31}H_{16}Cl_2N_2O_2$
			71.69	3.11	5.39	
2c	65	377-378	<u>61.19</u>	<u>2.61</u>	<u>4.56</u>	$C_{31}H_{16}Br_2N_2O_2$
			61.21	2.65	4.61	
2d	60	371-373	<u>52.97</u>	<u>2.32</u>	<u>3.95</u>	$C_{31}H_{16}I_2N_2O_2$
			53.02	2.30	3.99	
2e	59	363-365	<u>77.66</u>	<u>4.32</u>	<u>5.45</u>	$C_{33}H_{22}N_2O_4$
			77.63	4.34	5.49	
2f	63	370-372	85.12	4.08	5.07	C ₃₉ H ₂₂ N ₂ O ₂
			85.07	4.03	5.09	.,
2g	63	377-379	<u>48.56</u>	1.87	<u>3.70</u>	$C_{31}H_{14}Br_4N_2O_2$
			48.60	1.84	3.66	51 11 1 2 2
2h	57	369-371	82.80	5.81	5.70	C ₃₃ H ₂₂ N ₂ O ₂
			82.83	4.63	5.85	35 <u>22</u> <u>2</u> <u>2</u>
2i	66	372-374	62.24	3.14	4.36	$C_{33}H_{20}Br_2N_2O_2$
			62.29	3.17	4.40	55 20 2 2 2
4 a	66	247-249	73.95	4.41	4.86	C ₃₆ H ₂₆ N ₂ O ₆
			74.22	4.50	4.81	50 20 2 0
4b	43	251-253	66.35	3.66	4.27	C ₃₆ H ₂₄ Cl ₂ N ₂ O ₆
			66.37	3.71	4.30	50 24 2 2 0
4c	47	253-255	58.34	3.26	3.73	C ₃₆ H ₂₄ Br ₂ N ₂ O ₆
			58.40	3.27	3.78	50 27 2 2 0
4d	71	239-241	70.98	4.66	4.34	C ₃₈ H ₃₀ N ₂ O ₀
			71.02	4.71	4.36	- 30 30 2 8
4 e	71	235-237	64.58	3.69	4.43	C22H22N2OcS2
-		/	64.63	3.73	4.41	- 32222 - 60 2

Experimental

The IR spectra were measured on a Specord 75IR spectrophotometer in KBr pellets. The instrument was calibrated against polystyrene standards (v 1602 and 3003 cm⁻¹). The error of measurements was ± 2 cm⁻¹. The ¹H NMR spectra were recorded on a Varian VXR-200 Mercury spectrometer operating at 200 MHz in DMSO-d₆ with SiMe₄ as the internal standard; the δ scale was used in all cases.

The mass spectra were obtained on a Finnigan MAT 4615P instrument using a direct inlet system. The temperature of the ionization chamber was 180 °C, the ionization voltage was 70 eV, and the emission current was 100 μ A. The mass spectra of compounds **2e,f** and **5** were measured on an MSBKh time-of-flight mass spectrometer (PO Elektron, Sumy, Ukraine). The ionization was performed by bombardment with ²⁵²Cf fission fragments. The energy of ionizing particles was 90–110 MeV. The tube length was 45 cm, the accelerating voltage was 20 kV, and the accumulation time was 15–20 min.

The reaction products were purified by crystallization from the corresponding solvents. The progress of the reactions was monitored and the purity of the compounds was checked by TLC on Silufol UV-254 plates using ethyl acetate, chloroform, toluene, or their mixtures as the eluents. The melting points were determined on a Kofler hot-stage apparatus.

The starting 3-(2-aryl-2-oxoethylidene)oxindoles **1a**—i (see Refs 18 and 19) and *N*-acetyl derivative **3a** (see Ref. 19) were synthesized according to procedures described earlier. *N*-Acetyl derivatives **3b**—e were synthesized analogously and were used without isolation from the reaction mixtures.

6-Benzoyl-7-phenylindolo[**3**,**4**-*jk*]**phenanthridin-5**(**4***H*)-**one** (**2a**). *A*. A solution of 3-(2-oxo-2-phenylethylidene)oxindole (**1a**) (0.5 g, 2 mmol) in DMF (0.5 mL) was heated to 150 °C for 1 h, resulting in precipitation. Benzene (20 mL) was added to the reaction mixture, and compound **2a** was filtered off. The yield was 0.28 g (62%), m.p. 374—376 °C (from DMF). Found (%): C, 82.31; H, 3.89; N, 6.34. C₃₁H₁₈N₂O₂. Calculated (%): C, 82.66; H, 4.03; N, 6.22. IR (KBr), v/cm⁻¹: 3152 (NH); 1692 (C=O); 1665 (C=O); 1632(C=C). ¹H NMR (DMSO-d₆), δ: 9.21 (d, 1 H, H(12), J = 7.9 Hz); 8.74 (d, 1 H, H(1), J = 8.5 Hz); 8.31 (d, 1 H, H(9), J = 7.9 Hz); 7.83—8.05 (m, 3 H, H(2), H(10), H(11)); 7.08—7.57 (m, 9 H, H(3), Ar); 6.81 (br.s, 1 H, Ar); 6.51 (br.s, 1 H, Ar); 11.06 (s, 1 H). MS (EI, 70 eV), m/z (I_{rel} (%)): 450 [M]⁺ (8), 373 [M - C₆H₅]⁺ (5), 345 [M - Bz]⁺ (57), 105 [Bz]⁺ (100).

Compounds **2b**—**i** were synthesized according to an analogous procedure. The yields, physicochemical characteristics, and spectroscopic data for these compounds are summarized in Tables 1—3 and 8.

B. A solution of compound 5 (0.5 g, 1 mmol) in DMF (2 mL) was heated to 150 °C for 1 h. Then the reaction mixture was cooled, and compound **2a** was filtered off. The yield was 0.4 g (89%). The physicochemical and spectroscopic data for this compound are identical to those for compound **2a**, which was synthesized by heating 3-(2-oxo-2-phenylethylidene)oxindole (**1a**) in DMF.

1,1-Diacetyl-3,4-dibenzoyl-1,2,2a,3,4,5-hexahydrospiro-[benz[*cd*]indol-5,3 '-indoline]-2,2 '(1*H*)-dione (4a). *A*. A solution of *N*-acetyl-3-(2-oxo-2-phenylethylidene)oxindole (3a) (0.5 g, 1.7 mmol) in DMF (1 mL) was heated to 150 °C for 1 h. Then a 70% ethanolic solution (10 mL) was added, the reaction mixture was heated for 10 min, and compound 4a was filtered off. The yield was 0.3 g (60%), m.p. 247 °C (from AcOEt). **B.** A solution of 3-(2-oxo-2-phenylethylidene)oxindole (**2a**) (0.5 g, 2 mmol) in acetic anhydride (4 mL) was heated for 4 h. Then a 70% ethanolic solution (10 mL) was added, the reaction mixture was heated for 10 min, and compound **4a** was filtered off. The yield was 0.33 g (66%), m.p. 247–249 °C (from AcOEt). Found (%): C, 73.95; H, 4.86; N, 4.41. $C_{36}H_{26}N_2O_6$. Calculated (%): C, 74.22; H, 4.50; N, 4.81. IR (KBr), v/cm⁻¹: 1765 (C=O); 1717 (C=O); 1673 (C=O); 1600 (C=C). ¹H NMR (DMSO-d₆), δ : 2.25 (s, 3 H, CH₃ (Ac)); 2.46 (s, 3 H, CH₃ (Ac)); 4.44 (d, 1 H, H(5a), J= 10.5 Hz); 4.97–5.07 (m, 2 H, H(6), H(7)); 6.37 (d, 1 H, H(2) 6-aroyl, J = 8.5 Hz); 7.10 (d, 2 H, Ar, J = 7.8 Hz); 7.16–7.21 (m, 2 H, Ar); 7.27–7.37 (m, 4 H, Ar); 7.51–7.55 (m, 4 H, Ar); 7.66 (t, 1 H, Ar, J = 7.8 Hz); 7.82 (d, 1 H, Ar, J = 7.8 Hz); 7.87 (d, 1 H, Ar, J = 7.8 Hz); 8.24 (d, 2 H, Ar, J = 8.5 Hz).

Compounds **4b**—**e** were synthesized according to the method **B**. The physicochemical and spectroscopic data for these compounds are summarized in Tables 1 and 5.

3,4-Dibenzoyl-1,2,2a,3,4,5-hexahydrospiro[benz[*cd*]indole-5,3'-indoline]-2,2'(1'*H*)-dione (5) was synthesized from diacetyl derivative 4a by the reaction with $\text{Et}_3\text{O}^+\text{BF}_4^-$ in CH_2Cl_2 according to a procedure described earlier.²⁰

Triethyloxonium tetrafluoroborate (0.8 g, 4 mmol) was added to a solution of compound **4a** (0.5 g, 0.8 mmol) in CH₂Cl₂ (30 mL). The reaction mixture was stirred for 2 h. The precipitate was filtered off and treated with an excess of an aqueous sodium bicarbonate solution. The residue was recrystallized from ethyl acetate (50 mL), and compound **5** was obtained in a yield of 0.2 g (55%), m.p. 327–329 °C (from DMF). Found (%): C, 77.02; H, 4.41; N, 5.57. C₃₂H₂₂N₂O₄. Calculated (%): C, 77.10; H, 4.45; N, 5.62. IR (KBr), v/cm⁻¹: 1742 (C=O); 1693 (C=O); 1666 (C=O); 1604 (C=C). ¹H NMR (DMSO-d₆), δ : 3.79 (d, 1 H, H(5a), J= 10.6 Hz); 4.42–4.54 (t, 1 H, H(6), J= 10.6 Hz); 4.71 (d, 1 H, H(7), J= 10.6 Hz); 5.99 (d, 1 H, H(2), 6-aroyl, J = 7.4 Hz); 6.60–6.69 (m, 2 H, Ar); 6.81–7.26 (m, 6 H, Ar); 7.63 (d, 1 H, Ar, J= 7.8 Hz); 7.86 (d, 1 H, Ar, J= 8.0 Hz); 7.97 (d, 1 H, Ar, J= 8.0 Hz); 8.32 (d, 1 H, Ar, J= 7.8 Hz); 10.43 (s, 1 H, NH); 10.68 (s, 1 H, NH). PDMS: m/z= 499 [M + H]⁺.

X-ray diffraction study. X-ray diffraction data for crystals of compound 2d were collected on an automated four-circle Siemens P3/PC diffractometer (Mo-K α radiation, graphite monochromator, $\theta/2\theta$ -scanning technique, $2\theta_{max} = 50^{\circ}$). The semiempirical ψ -scan absorption correction was applied ($T_{min} = 0.622$, $T_{max} = 0.762$). The structure was solved by direct methods using the SHELXTL program package²¹ and refined by the full-matrix least-squares method based on F^2 with anisotropic displacement parameters for nonhydrogen atoms. The hydrogen atoms were located in difference electron density maps and refined using a riding model with $U_{iso} = 1.2U_{equiv}$ of the parent nonhydrogen atoms. The atomic coordinates and complete tables of the bond lengths and bond angles were deposited with the Cambridge Structural Database (CCDC 249069).

X-ray diffraction data for crystals of compound **4a** were collected on a Xcalibur-3 diffractometer (Mo-K α radiation, CCD detector, graphite monochromator, ω -scanning technique, $2\theta_{max} = 50^{\circ}$). The structure was solved by direct methods with the use of the SHELXTL program package²¹ and refined by the full-matrix leastsquares method based on F^2 with anisotropic displacement parameters for nonhydrogen atoms. The hydrogen atoms were located in difference electron density maps and refined isotropically. The atomic coordinates and complete tables of the bond lengths and bond angles were deposited with the Cambridge Structural Database (CCDC 665531).

Parameter	2d	4 a
Molecular formula	$C_{31}H_{16}N_2O_2I_2$	C ₃₆ H ₂₆ N ₂ O ₆
Molecular weight	702.26	582.59
Unit cell parameters		
a/Å	19.50(1)	10.532(3)
b/Å	6.902(3)	12.654(3)
c/Å	19.51(1)	21.237(2)
β/deg	105.30(5)	100.79(1)
Crystal system	Monoo	elinic
Space group	$P2_1/n$	$P2_1/c$
Ζ	4	4
$V/Å^2$	2533(3)	2780(1)
<i>F</i> (000)	1352	1216
$d_{\rm calc}/{\rm g}{\rm cm}^{-3}$	1.842	1.392
$\mu(Mo-K\alpha)/mm^{-1}$	2.516	0.096
Number of measured/	4949/4418	11518/4773
independent reflections		
R _{int}	0.060	0.028
Number of refinement parameters	334	501
wR_2	0.170	0.077
$R_1 (I \ge 2\sigma(I))$	0.070	0.034
S	1.00	0.822

Table 9. Crystallographic characteristics and the X-ray data collection and refinement statistics for compounds 2d and 4a

Principal crystallographic characteristics and the X-ray data collection and refinement statistics for compounds **2d** and **4a** are given in Table 9.

References

- A. S. El-Ahl Abdel, H. Afeefy, M. A. Metwally, J. Chem. Res. Miniprint, 1994, 1, 201.
- 2. K. S. Joshi, R Jain, Heterocycles, 1990, 31, 473.
- A. Dandia, M. Upreti, B. Rani, U. C. Pant, I. J. Gupta, J. Fluorine Chem., 1998, 91, 171.

4. D. Du Puis, H. G. Lindwall, J. Am. Chem. Soc., 1934, 56, 471.

- 5. P. H. Zrike, H. G. Lindwall, *J. Am. Chem. Soc.*, 1935, **57**, 207.
- 6. R. S. Belen 'kaya, E. I. Boreko, M. N. Zemtsova, M. I. Kalinina, M. M. Timofeeva, P. L. Trakhtenberg, V. M. Chelnov, A. E. Lipkin, V. I. Votyakov, *Khim.-farm. Zh.*, 1981, **15**, No. 3, 29 [*Pharm. Chem. J.*, 1981, **15**, No. 3, 171 (Engl.Transl.)].
- A. C. Coda, G. Desimoni, P. P. Righetti, G. Tacconi, E. Dradi, *Gazz. Chim. Ital.*, 1983, **113**, 191.
- A. B. Serov, V. G. Kartsev, Yu. A. Aleksandrov, *Abstrs Intern. Conf. "Chemistry of Nitrogen Containing Heterocycles" (September 30—October 3, 2003)*, Kharkov, Ukraine, 2003, p. 258.
- C. G. Richards, D. E. Thurston, *Tetrahedron*, 1983, **39**, 1817.
 G. Tacconi, A. C. Piccolini, P. P. Righetti, E. Selva, G. Desi-
- moni, J. Chem. Soc., Perkin Trans. 1, 1976, 1248.
 11. P. Bamfield, A. W. Jonson, A. F. Katner, J. Chem. Soc. (C), 1966, 1028.
- A. Kubo, T. Nakai, T. Nozoye, A. Itai, Y. IItaka, *Heterocycles*, 1978, 9, 1051.
- A. Itai, Y IItaka, A. Kubo, *Acta Crystallogr., Sect. B*, 1978, 34, 3775.
- H. Günter, NMR-Spectroscopie, Georg Thieme Verlag, Stuttgart, 1973.
- Yu. V. Zefirov, *Kristallografiya*, 1997, **42**, 936 [*Crystallogr. Repts.*, 1997, **42** (Engl. Transl.)].
- H. B. Burgi, J. D. Dunitz, *Structure Correlation*, 2, VCH, Weinheim, 1994, p. 741.
- N. S. Zefirov, V. A. Palyulin, E. E. Dashevskaya, J. Phys. Org. Chem., 1990, 3, 147.
- H. G. Lindwall, J. S. Maclennan, J. Am. Chem. Soc., 1932, 54, 4739.
- G. Tacconi, P. Iadarola, F. Marinone, P. P. Righetti, G. Desimoni, *Tetrahedron*, 1975, 31, 1179.
- 20. S. Hanessian, Tetrahedron Lett., 1967, 1549.
- G. M. Sheldrick, SHELXTL PLUS. PC Version. A System of Computer Programs for the Determination of Crystal Structure from X-ray Diffraction Data, Rev. 5.1, 1998.

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