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CRYSTAL AND MOLECULAR STRUCTURE OF 6-METHYL-2,7-DIPHENYL-1,3-

DIFORMYLINDOLIZINE

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An x-ray crystallographic investigation was made of 6-methyl-2,7-diphenyl-1,3diformylindolizine, obtained by the formylation of 6-methyl-2,7-diphenylindolizine. The effect of various carbonyl-containing substituents at positions 1 and 3 on the geometry of the indolizine ring in the structually investigated indolizine derivatives is discussed.

6-Methyl-2,7-diphenyl-1,3-diformylindolizine (I) was obtained by the formylation of 6-methyl-2,7-diphenylindolizine by the Vilsmeier reaction.



In view of the electrophilic character of this reaction it could be expected that formylation would take place at positions 1 and 3 of the indolizine ring. In order to obtain conclusive evidence for the structure of (I) we undertook its x-ray crystallographic investigation.

The general appearance of the molecule of (I), the numbering of the atoms, the bond lengths, and the bond angles are shown in Fig. 1. The five- and six-membered rings of the indolizine system in the molecule of (I) are planar within the limits of 0.012(8) and 0.025 (8) Å respectively. The dihedral angle between the planes of the rings is 3.5° , while the maximum deviation of the atoms from the mean-square plane of the whole bicyclic system amounts to only 0.051 (8) Å (for the C₍₆₎ atom). Subsequently, therefore, we will consider the orientation of the substituents in relation to this plane, drawn through all the indolizine rings as a whole.

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TABLE 1. The Bond Lengths in the Bicyclic Ring of the Indolizine Derivatives



Com- pound*	1-2	23	3-N ₍₄₎	N (4)-5	56	6-7	78	8—9	9—1 -	N ₍₄₎ -9	Refer- ence
I	1,41	1,40	1,42	1,38	1,37	1;42	1,37	1,40	1,43	1,39	Present work
II † IV † VI VI VII VIII	1,420 1,426 1,395 1,402 1,427 1,427 1,427 1,44 1,44	1,393 1,384 1,401 1,385 1,376 1,390 1,37 1,37	1,397 1,407 1,414 1,384 1,352 1,41 1,38	1,385 1,382 1,368 1,368 1,369 1,395 1,38 1,43	1,373 1,365 1,360 1,353 1,347 1,346 1,40 1,40	1,402 1,411 1,404 1,404 1,425 1,402 1,41 1,41	1,348 1,367 1,359 1,354 1,355 1,381 1,39 1,34	1,425 1,393 1,437 1,431 1,421 1,421 1,421 1,44 1,46	1,369 1,375 1,374 1,378 1,354 1,375 1,34 1,37	1,410 1,410 1,388 1,394 1,422 1,419 1,42 1,42	[1] [4] [3]

*(IV) is di(2,8-diphenyl-3-indolizinyl)disulfide, (V) is 2phenyl-6-nitroindolizine, (VI) is 2-phenyl-8-nitroindolizine, (VII) is 2-phenyl-5-butylamino-8-nitroindolizine, and (VIII) is 2-phenyl-5-piperidino-8-nitroindolizine. †Contains two indolizine rings in the molecule.



Fig. 1. The data from x-ray crystallographic analysis; the bond lengths and bond angles in the molecule of (I).

Among the few structurally investigated derivatives of indolizine there are only two compounds with carbonyl-containing (benzoyl) substituents, i.e., 1,1-bis(5-methyl-2-phenyl-1-benzoyl-3-indolizinyl)ethylene (II) [1] and 1-(2-pyridyl)-3-benzoyl-6-bromoindolizine (III) [2]. Both papers consider the contribution to the geometry of the molecules from forms with separation of charges, which for indolizine (I) can be represented, for example, in the following way:



On the basis of the chemical and spectral data it was supposed that the molecule of (III) exists predominantly in the bipolar form (B, C), but the x-ray crystallographic data obtained in [2] cannot, in our opinion, provide reliable evidence for this proposal on account of their insufficiently high accuracy. (The errors amount to 0.05 Å in the determination of the bond lengths and 3° in the bond angles.) These data will not therefore be used in the subsequent discussion.

Atom	x	y .	z	B ^{eq} iso
Atom $O_{(1)}$ $O_{(2)}$ $N_{(4)}$ $C_{(2)}$ $C_{(3)}$ $C_{(5)}$ $C_{(5)}$ $C_{(5)}$ $C_{(5)}$ $C_{(5)}$ $C_{(10)}$ $C_{(11)}$ $C_{(12)}$ $C_{(13)}$ $C_{(13)}$ $C_{(15)}$ $C_{(16)}$ $C_{(17)}$ $C_{(18)}$ $C_{(22)}$ $C_{(22)}$ $C_{(22)}$ $C_{(22)}$ $C_{(22)}$	6421 (6) 4901 (7) 4933 (7) 5534 (8) 6260 (8) 5927 (8) 4199 (9) 3251 (8) 3062 (8) 3062 (8) 3763 (8) 4698 (8) 6596 (8) 5558 (9) 2143 (9) 1005 (11) 96 (9) 356 (12) 1509 (13) 2380 (9) 7210 (9) 7200 (8) 7883 (10) 8923 (12) 9114 (10) 8261 (9)	457 (4) 4829 (4) 2190 (4) 3301 (5) 2499 (6) 1810 (6) 1759 (5) 2240 (6) 3182 (6) 3593 (5) 3095 (6) 959 (6) 4167 (6) 3736 (6) 4155 (6) 4683 (6) 4794 (7) 4385 (7) 3852 (6) 2380 (6) 1631 (6) 1524 (6) 2138 (8) 2872 (7) 2996 (6)	$\begin{array}{c} 521 (5)\\ 2055 (5)\\ 592 (6)\\ 1876 (7)\\ 2236 (7)\\ 1442 (7)\\ -326 (7)\\ -326 (7)\\ -326 (7)\\ 1442 (7)\\ -869 (7)\\ 71 (7)\\ 829 (7)\\ 1341 (8)\\ 2448 (8)\\ -1682 (9)\\ -1333 (7)\\ -2083 (10)\\ -3155 (10)\\ -3155 (10)\\ -3520 (8)\\ 3300 (7)\\ 3992 (8)\\ 5023 (9)\\ 5551 (9)\\ 4662 (10)\\ 3609 (8)\end{array}$	$\begin{array}{c} {}^{2} \text{iso} \\ \hline \\ 4,5(2) \\ 5,3(2) \\ 2,7(2) \\ 2,7(3) \\ 2,8(3) \\ 2,6(3) \\ 3,1(3) \\ 3,0(3) \\ 3,3(3) \\ 2,6(3) \\ 2,8(3) \\ 2,7(3) \\ 3,3(3) \\ 3,3(3) \\ 3,3(3) \\ 3,9(3) \\ 3,9(3) \\ 3,9(3) \\ 3,8(3) \\ 4,7(4) \\ 5,2(4) \\ 5,2(4) \\ 5,2(4) \\ 5,2(4) \\ 5,2(4) \\ 5,2(4) \\ 5,6(4) \\ 3,8(3) \end{array}$
C(24)	2379(8)	1716(6)	-2023(7)	4,1(3)

TABLE 2. The Coordinates of the Nonhydrogen Atoms (\times 10⁴) and Their Equivalent Isotropic Temperature Factors (A²)

TABLE 3. The Coordinates of the Hydrogen Atoms $(\times 10^3)$

Atom	x	y	z	Atom	x	y	z
H(5) H(8) H(10) H(11) H(13) H(14) H(15) H(16) H(17)	440 357 735 620 79 - 82 - 36 169 325	101 433 72 425 407 503 521 451 351	-50 26 208 329 -45 -180 -377 -442 -308	$H_{(19)} \\ H_{(20)} \\ H_{(21)} \\ H_{(22)} \\ H_{(23)} \\ H_{(24.1)} \\ H_{(24.2)} \\ H_{(24.3)}$	618 778 962 990 849 253 250 127	112 92 206 341 355 100 200 183	374557617496301-198-275-210

Substitution of the benzoyl groups in the molecule of (II) by the more electronegative aldehyde groups in the indolizine (I) should lead to shortening of the $C_{(1)} - C_{(11)}$ and $C_{(3)}$ $C_{(1,0)}$ bonds on account of the larger contribution from forms B and C. It can evidently be considered that such a tendency is observed within the accuracy limits in the determination of the geometric parameters for the molecule of (I). In fact, the average length of the C(in-dolizine)-C(benzoyl) bond in (II) amounts to 1.460 Å, whereas the lengths of the $C_{(1)}-C_{(11)}$ and $C_{(3)} - C_{(10)}$ bonds in the molecule of (I) are 1.43(1) and 1.44(1) Å. Unfortunately, unsubstituted indolizine has not been investigated structurally. (An attempt to obtain its single crystals proved unsuccessful [3]). For this reason it is impossible to determine what changes occur in the geometry of the indolizine ring with the introducton of the carbonyl-containing substituents at positions 1 and 3. As seen from Table 1, which gives the bond lengths in the bicyclic rings of the structurally investigated indolizine derivatives, the lengths of the respective bonds in the various molecules vary greatly (e.g., for the $N_{(4)}$ - $C_{(3)}$ distance, from 1.35 to 1.42 Å). Compounds (I-VIII) differ greatly in the number, position, and nature of the substituents in the indolizine ring. However, it can be seen that some shortening of the $C_{(8)} - C_{(9)}$ and $N_{(4)} - C_{(9)}$ bonds and elongation of the $C_{(1)} - C_{(9)}$ bond are observed in the indolizine (I) compared with the molecules of (V-VIII) nct containing substituents at positions 1 and 3. This is due to the contribution from the forms with separation of the charges.

In the molecule of (III), where there is no substituent at position 2 of the indolizine ring, the carbonyl group lies in the plane of this ring. In (II) the planes of carbonyl groups at positions 1 are rotated in relation to the planes of the indolizine systems by 17 and 37°. This is probably due to intramolecular contacts between the substituents at positions 1 and 2. In the investigated molecule of (I), compared with the molecule of (II), the bulky benzoyl group at position 1 is substituted by an aldehyde group, the plane of which forms a dihedral angle of 5.0°, [smaller than in the molecule of (II)] with the plane of the bicyclic system. The angle formed by the plane of the second aldehyde group at position 3 amounts to 14.7°. The different orientations of the aldehyde groups in the molecule of (I) are evidently determined by the asymmetry of the indolizine ring [in particular, by the inequality of the angles $C_{(1)}C_{(8)}C_{(8)}$ 134.4 (8)° and $C_{(3)}N_{(4)}C_{(5)}$ 128.2 (7)°], on account of which even with larger rotation of the 3-aldehyde group the $O_{(1)} \ldots C_{(5)}$ 2.98 (1)Å distance remains smaller than $O_{(2)} \ldots C_{(8)}$ 3.07 (1)Å. In addition, the steric interactions between the substituents at participation of the second tween the substituents at positions 1, 2, and 3 in the molecule of (I) lead to an increase in the $C_{(2)}C_{(1)}C_{(11)}$ 128.1 (8) and in the $C_{(2)}C_{(3)}C_{(10)}$ angle to 12.8 (8)° compared with the theoretical value of 126° and to rotation of the plane of the phenyl ring at position 2 by 48.4° in relation to the plane of the indolizine system. The plane of the other phenyl substituent forms a dihedral angle of 61.3° with the plane of the indolizine ring.

EXPERIMENTAL

The PMR spectrum was obtained on a Tesla BS-487 spectrometer at 80 MHz in deuterochloroform with TMS as internal standard. The IR spectrum was recorded in tablets with potassium bromide on a UR-20 instrument. The UV spectrum was recorded in chloroform on a Specord UV-vis instrument. The mass spectrum was measured on a MX-1303 mass spectrometer at 70 V.

The crystals of the indolizine (I) $C_{23}H_{17}NO_2$ are monoclinic; a = 9.8831 (6), b = 14.692 (1), c = 11.972(1) Å, $\beta = 98.373(6)^{\circ}$, Z = 4 (at 20°C), space group $P2_1/c$. The unit cell parameters and the intensities of 1779 unique reflections, 1009 of which with $I \ge 2\sigma$ were used in the calculations, were measured on a Hilger-Watts automatic four-circle diffractometer (λCuK_{α} , graphite monochromator, $\theta/2\theta$ scan, $\theta \le 66^{\circ}$). The structure was interpreted by the direct method by MULTAN program and refined by the full-matrix method of least squares in anisotropic approximation for the nonhydrogen atoms. The hydrogen atoms of the methyl group were revealed from a difference synthesis, and the remaining hydrogen atoms were placed at the calculated positions; all the hydrogen atoms were included in the calculation with fixed position and temperature parameters ($B_{1SO} = 6$ Å²). The final values of the divergence factors were R = 0.069 and R_w = 0.064. All the calculations were made on an Eclipse S/200 computer by means of the INEXTL programs [5].

The coordinates of the nonhydrogen atoms are given in Table 2, and the coordinates of the hydrogen atoms are given in Table 3.

<u>6-Methyl-2,7-diphenyl-1,3-diformylindolizine</u>. To 1.1 ml (12 mmole) of phosphorus oxychloride at room temperature we added 5 ml of DMFA. We then gradually added a solution of 1.4 g (5 mmole) of 6-methyl-2,7-diphenylindolizine [6] in 10 ml of DMFA. The mixture was stirred at room temperature for 40 min, at 45-50°C for 1 h, and at 80°C for 2 h. It was then poured onto ice and neutralized with a 50% solution of potassium carbonate. The precipitate was filtered off, washed with water, and dried. We isolated 0.76 g (50%) of 6-methyl-2,7-diphenyl-1,3-diformylindolizine; mp 192-194°C (from isopropyl alcohol). PMR spectrum: 9.82 (2H, s, 3-CHO, 5H); 9.64 (1H, s, 1-CHO); 8.50 (1H, s, 8-H); 2.36 ppm (3H, s, 6-CH₃). IR spectrum: 1655 cm⁻¹ ($\nu_{C=O}$). UV spectrum, λ_{max} (log ε): 246 (4.37); 278 (4.60); 294 (4.42); 302 (4.40); 362 nm (4.42). Found %: C 81.6; H 5.1; N 4.3; M⁺ 339. C₂₃H₁₇NO₂. Calculated %: C 81.4; H 5.0; N 4.1%.

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MASS-SPECTROMETRIC BEHAVIOR OF ISATIN OXIMES

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On the basis of an analysis of the mass spectra of a large series of benzo-substituted isatin oximes it is shown that their molecular ions undergo type II Beckmann rearrangment to the corresponding o-N-carboxyaminobenzonitriles.

It is known that, like many benzolactams [1], oxindole under electron impact loses a molecule of CO with the formation of an ion that has a structure similar to that of a 2-methyl nitrene, since its subsequent fragmentation coincides with the fragmentation of the $[M - N_2]^+$ ion of a 2-methyl azide [2]. The fragmentation of the molecular ion (M^+) of isatin is also determined by primary elimination of a molecule of CO, chiefly from the 2 position [3-5]. The same primary fragmentation process (the loss of CO) is also characteristic for the M^+ ions of 3-aryl-iminoisatins [5] and isatin 3-thiosemicarbazones [6]. Up until now, the mass-spectrometric behavior of isatin-3-oximes has not been investigated, even though it is known that such 3-hydroxyiminolactams may exist in several tautomeric forms [7], and thermal type II Beckmann rearrangement, which takes place at temperatures above 200°C [8-11] in vacuo [10] and leads to o-aminobenzonitriles, has been observed for isatin oximes. Since transformations of M^+ ions that are similar to certain reactions of the same compounds in the condensed phase are frequently observed under the conditions of mass-spectrometric experiments [12-15], we studied the behavior of a series of isatin 3-oximes I-XII under electron impact.



An M⁺ peak, the intensity of which (Table 2) depends to a considerable degree on the character of the substituent and its position in the benzene ring, is observed in the mass

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