

HETEROCYCLES WITH A BRIDGING NITROGEN ATOM.

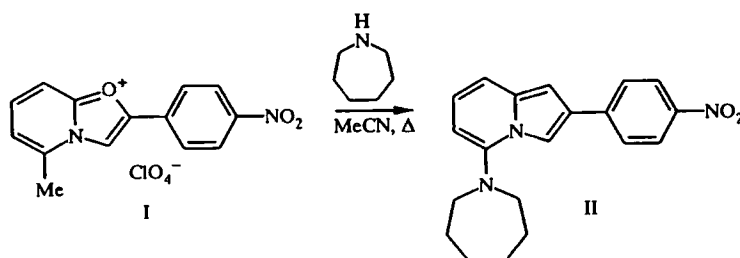
9.* RECYCLIZATION OF AN OXAZOLE FRAGMENT TO A PYRROLE FRAGMENT. SYNTHESIS AND CRYSTAL STRUCTURE OF 5-HEXAMETHYLENIMINO-2-*p*-NITROPHENYLINDOLYZINE

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*X-ray diffraction structural analysis was used to determine the structure of 5-hexamethylenimino-2-*p*-nitrophenylindolyzine formed in the reaction of 5-methyl-2-*p*-nitrophenyloxazolo[3,2-*a*]pyridinium perchlorate with hexamethylenimine.*

We have theoretically predicted [2] and then experimentally discovered a previously unreported class of oxazole-pyrrole recyclizations in the case of the transformation of 5-methyloxazolo[3,2-*a*]pyridines into indolyzines [1, 3]. The structure of the indolyzine products was demonstrated by spectral methods. In the present communication, we finally confirmed the formation of the indolyzine skeleton during recyclization using x-ray diffraction structural analysis.

The recyclization took place upon heating oxazopyridinium salt I with hexamethylenimine in acetonitrile at reflux to give aminoindolyzine II in 65% yield.



The x-ray diffraction structural data of the indicated indolyzine are given in Tables 1 and 2 and its structure is shown in Fig. 1.

The twist of the phenyl ring relative to the plane of the bicyclic system is $18.5 \pm 2.8^\circ$, while the nitro group is twisted by $-16.3 \pm 3.1^\circ$ relative to the benzene ring. Marked alternation of single and double bonds typical for indolyzines as a whole is found in the six-membered ring of the indolyzine system in II [4]. Such alternation is not pronounced for the five-membered ring in the bicyclic system. Although the dialkylamino group is bound to the most electron-deficient atom of the indolyzine system, marked conjugation of the unshared pair of this group with the heterocycle is nevertheless not observed in this system. Firstly, the hexamethylenimine fragment is twisted by $23.7 \pm 2.6^\circ$ relative to the plane of the indolyzine system. Secondly, an interesting feature is found by comparing the lengths of the single and double bonds in the six-membered ring in II with the reported values for other indolyzines [5]. Greater alternation of the bond lengths (deviation from the ordinary C-C aro-

*For Communication 8, see [1].

TABLE 1. Bond Lengths d (Å) in II

Bond	d	Bond	d
O(1)—N(1)	1,14(3)	C(8)—N(8)	1,42(2)
O(2)—N(1)	1,20(2)	N(8)—C(16)	1,45(2)
N(1)—C(13)	1,58(2)	N(8)—C(21)	1,52(2)
C(1)—C(2)	1,40(2)	C(10)—C(11)	1,34(2)
C(1)—N(9)	1,39(2)	C(10)—C(15)	1,41(2)
C(2)—C(3)	1,40(1)	C(11)—C(12)	1,40(2)
C(2)—C(10)	1,48(2)	C(12)—C(13)	1,37(2)
C(3)—C(4)	1,38(2)	C(13)—C(14)	1,29(2)
C(4)—C(5)	1,42(2)	C(14)—C(15)	1,43(2)
C(4)—N(9)	1,42(2)	C(16)—C(17)	1,54(3)
C(5)—C(6)	1,34(2)	C(17)—C(18)	1,40(3)
C(6)—C(7)	1,41(2)	C(18)—C(19)	1,53(3)
C(7)—C(8)	1,33(2)	C(19)—C(20)	1,44(3)
C(8)—N(9)	1,41(2)	C(20)—C(21)	1,57(2)

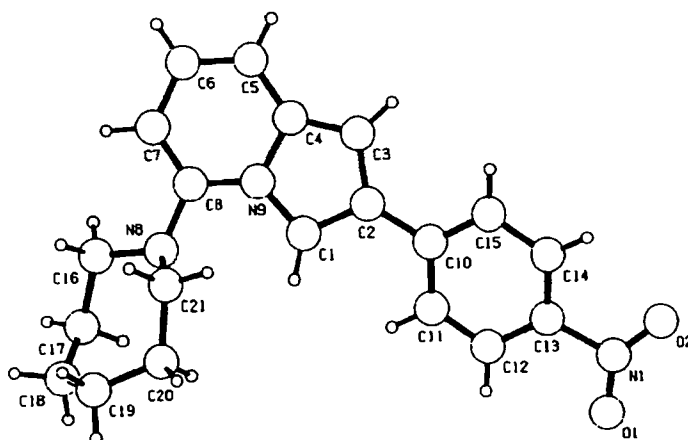


Fig. 1. Numbering of atoms and structure of compound studied.

matic bond) for II than for any other reported case. The longest single bonds and shortest double bonds among indolyzines studied were found in the pyridine ring in II. In other words, there is no conjugation of the unshared pair of the NR_2 group, which would have led to levelling of the bond lengths in the skeleton.

EXPERIMENTAL

5-Hexamethylenimino-2-*p*-nitrophenylindolyzine (II). A sample of 0.1 mmole 5-methyl-2-*p*-nitrophenyloxazolo-[3,2-*a*]pyridinium perchlorate (I) [3] with 5 ml hexamethylenimine in 15 ml acetonitrile was heated at reflux for 3 h. The reaction mixture was poured into water. The orange crystalline precipitate was filtered off to give II in 65% yield, mp 133°C. Found: C, 71.0; H, 6.4%. Calculated for $\text{C}_{20}\text{H}_{21}\text{N}_3\text{O}_2$: C, 71.6; H, 6.3%. The PMR and mass spectral data are in complete accord with the structure and will be presented in a communication devoted to the spectral features of 5-substituted indolyzines.

The x-ray diffraction structural investigation of 5-hexamethylenimino-2-*p*-nitrophenylindolyzine was carried out on an automatic CAD-4 monocrystal diffractometer using λMoK_α radiation. The unit cell parameters were for θ angles in the 12-13° range using 25 reflections. The unit cell parameters for the monoclinic crystals: $a = 6.614(1)$, $b = 15.006(1)$, $c = 8.821(1)$ °, $\beta = 102.94(2)$ °, $Z = 2$, space group Pn. The structure was solved by the direct method and refined by the method of least squares using the SHELXL-93 program package [6] isotropically for the nonhydrogen atoms. The coordinates of the hydrogen

TABLE 2. Bond Angles ω (deg) in II

Bond angle	ω	Bond angle	ω
O(1)—N(1)—O(2)	135(3)	C(1)—N(9)—C(4)	109(2)
O(1)—N(1)—C(13)	118(3)	C(1)—N(9)—C(8)	128(2)
O(2)—N(1)—C(13)	107(3)	C(4)—N(9)—C(8)	123(2)
C(2)—C(1)—N(9)	107(2)	C(11)—C(10)—C(15)	121(2)
C(1)—C(2)—C(3)	108(2)	C(11)—C(10)—C(2)	119(2)
C(1)—C(2)—C(10)	126(2)	C(15)—C(10)—C(2)	120(2)
C(3)—C(2)—C(10)	126(2)	C(10)—C(11)—C(12)	121(2)
C(4)—C(3)—C(2)	109(2)	C(13)—C(12)—C(11)	117(2)
C(3)—C(4)—C(5)	138(2)	C(14)—C(13)—C(12)	125(2)
C(3)—C(4)—N(9)	106(2)	C(14)—C(13)—N(1)	119(2)
C(5)—C(4)—N(9)	116(2)	C(12)—C(13)—N(1)	116(2)
C(6)—C(5)—C(4)	123(2)	C(13)—C(14)—C(15)	120(2)
C(5)—C(6)—C(7)	117(2)	C(10)—C(15)—C(14)	117(2)
C(8)—C(7)—C(6)	125(2)	N(8)—C(16)—C(17)	111(2)
C(7)—C(8)—N(9)	116(2)	C(18)—C(17)—C(16)	117(2)
C(7)—C(8)—N(8)	131(2)	C(17)—C(18)—C(19)	120(3)
N(9)—C(8)—N(8)	113(2)	C(20)—C(19)—C(18)	121(3)
C(8)—N(8)—C(16)	114(2)	C(19)—C(20)—C(21)	114(2)
C(8)—N(8)—C(21)	110(2)	N(8)—C(21)—C(20)	110(2)
C(16)—N(8)—C(21)	114,3(1)		

atoms were calculated geometrically and refined in rigid coupling with the corresponding carbon atom. The final R factor was 0.0658 using 595 independent reflections with $I > 2\sigma(I)$. The positional parameters of the atoms in the compound studied and their isotropic temperature parameters were deposited at the Cambridge Structural Data Bank.

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