Molecular Structure of a Novel Indole Derivative, (2*SR*,3a*SR*)-2-Phenyl-2,3,3a,4-tetrahydro-1*H*-pyrazolo[1,5-*a*]indole

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The molecular structure of the novel indole derivative, (2*SR*,3a*SR*)-2-phenyl-2,3,3a,4-tetrahydro-1*H*-pyrazolo[1,5-*a*]indole which was obtained from 2-allylphenylhydrazone was established by X-ray diffraction methods.

Keywords molecular structure; pyrazol[1,5-*a*]indole; X-ray analysis; novel indole

In studies[1)] of the amino-Claisen rearrangement of ethyl-7-allylindole-2-carboxylate **1** (Chart 1), it has been found that Fisher indolization of the hydrazone **2** gave the 1*H*-pyrazolo[1,5-*a*]indole **3** without giving the indole **1** expected from the usual cyclization. This intramolecular cycloaddition provides a novel synthetic method for 2,3,3a,4-tetrahydro-1*H*-pyrazolo[1,5-*a*]indole derivatives, but we could not unambiguously determine the molecular structure of **3** from the NMR, IR, and MS (mass spectral) data. In order to elucidate the molecular structure and the details of the stereochemistry of **3**, the X-ray diffraction investigation of **3** derived from **4** and **5** has been undertaken. The information obtained from the X-ray studies was correlated with the data from the NMR, IR, and MS spectra completely.[1)]

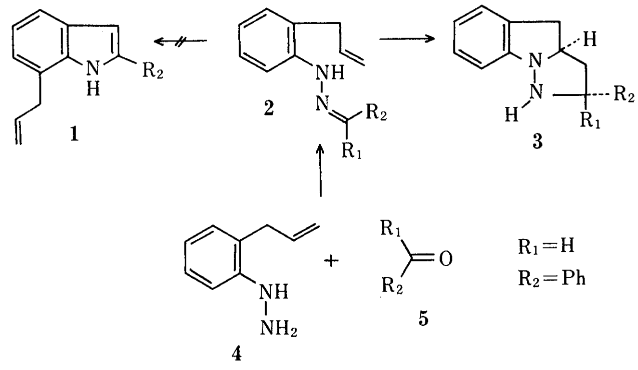

Chart 1

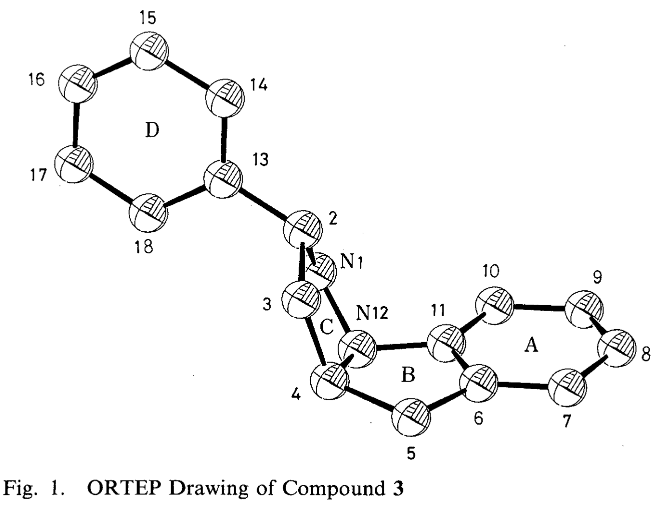

Fig. 1. ORTEP Drawing of Compound **3**

Results and Discussion

The molecular structure and the atomic numbering are presented in Fig. 1 as an ORTEP[2)] drawing. The bond lengths and bond angles are given in Table III together with their estimated standard deviations in parentheses. The average C–C lengths of the two benzene rings are 1.388 and 1.385 Å, respectively, which are compared well with the normal value of 1.395 Å. As shown in Fig. 1, the 1*H*-pyrazolo[1,5-*a*]indole part of **3** has an envelope form in the crystal structure. The deviation from the least-squares planes through portions of the molecule were calculated (Table IV); the dihedral angle between the least-squares planes defined by the tetrahydroindole ring (ring A and B) and the pyrazole ring (ring C) is 67.1°, and that between the tetrahydroindole ring and the phenyl ring (ring D) is

TABLE I. Crystal Data

Formula	$C_{16}H_{16}N_2$
Space group	$P2_1/c$
Cell parameters	$a=10.272$ (2), $b=16.692$ (1), $c=7.716$ (3), $\beta=84.76°$
Z-value	4
Volume	1317.5 Å^3

TABLE IIa. Atomic Parameters for Non-hydrogen Atoms

	x	y	z	B_{eq}
N1	0.4884 (2)	0.3983 (3)	0.0629 (2)	3.94
C2	0.4723 (2)	0.3658 (2)	0.2425 (3)	4.94
C3	0.3675 (3)	0.4162 (3)	0.3421 (3)	8.50
C4	0.3052 (3)	0.4678 (2)	0.2102 (2)	4.83
C5	0.1582 (2)	0.4547 (2)	0.2019 (2)	5.88
C6	0.1517 (2)	0.4004 (3)	0.0489 (3)	4.42
C7	0.0466 (2)	0.3600 (2)	−0.0124 (2)	5.71
C8	0.0694 (2)	0.3112 (3)	−0.1590 (3)	6.05
C9	0.1927 (3)	0.3032 (2)	−0.2445 (2)	5.40
C10	0.2999 (2)	0.3435 (3)	−0.1851 (3)	4.58
C11	0.2763 (3)	0.3912 (2)	−0.0383 (3)	3.69
C12	0.3695 (2)	0.4392 (2)	0.0366 (2)	3.67
C13	0.6005 (3)	0.3631 (2)	0.3251 (2)	4.21
C14	0.6864 (2)	0.4283 (2)	0.3124 (3)	4.68
C15	0.8033 (2)	0.4250 (2)	0.3911 (2)	5.86
C16	0.8330 (3)	0.3581 (3)	0.4833 (2)	6.98
C17	0.7483 (2)	0.2947 (2)	0.4989 (2)	7.22
C18	0.6318 (3)	0.2960 (3)	0.4195 (3)	5.78

The estimated standard deviations are shown in parentheses.

$$B_{eq}=(4/3)\sum_i\sum_j Bij\cdot ai\cdot aj$$

TABLE IIb. Fractional Coordinates and Isotropic Thermal Parameters (Å^2) for Hydrogen Atoms

	x	y	z	B_{iso}
HC1	0.5418 (4)	0.4237 (4)	0.0408 (4)	2.5
HC2	0.4423 (4)	0.3110 (4)	0.2337 (4)	4.6
HC3A	0.3930 (4)	0.4530 (4)	0.4372 (4)	6.4
HC3B	0.2973 (3)	0.3821 (4)	0.4050 (4)	8.3
HC4	0.3273 (4)	0.5301 (5)	0.2176 (5)	4.1
HC5A	0.1176 (4)	0.4220 (4)	0.3058 (5)	4.8
HC5B	0.1182 (4)	0.4998 (4)	0.1712 (5)	5.9
HC7	−0.0404 (4)	0.3714 (4)	0.0460 (4)	4.6
HC8	0.0053 (4)	0.2745 (4)	−0.1992 (4)	6.5
HC9	0.2024 (4)	0.2729 (4)	−0.3418 (4)	4.5
HC10	0.3879 (4)	0.3453 (4)	−0.2358 (4)	3.6
HC14	0.6678 (4)	0.4814 (4)	0.2614 (4)	3.3
HC15	0.8570 (4)	0.4727 (4)	0.3704 (4)	4.6
HC16	0.9234 (3)	0.3520 (4)	0.5181 (4)	5.3
HC17	0.7689 (4)	0.2469 (4)	0.5456 (4)	5.8
HC18	0.5766 (4)	0.2429 (4)	0.4221 (4)	4.5

TABLE III. Bond Lengths (Å) and Angles (°)

N1–C2	1.483 (3)	N1–N12	1.430 (4)
C2–C3	1.519 (4)	C2–C13	1.515 (4)
C3–C4	1.519 (4)	C4–C5	1.533 (4)
C4–N12	1.516 (3)	C5–C6	1.495 (4)
C6–C7	1.392 (4)	C6–C11	1.399 (4)
C7–C8	1.396 (4)	C8–C9	1.380 (4)
C9–C10	1.403 (4)	C10–C11	1.388 (4)
C11–N12	1.412 (4)	C13–C14	1.399 (4)
C13–C18	1.390 (5)	C14–C15	1.395 (3)
C15–C16	1.373 (5)	C16–C17	1.368 (5)
C17–C18	1.393 (4)		
C2–N1–N12	106.5 (2)	N1–C2–C3	106.5 (3)
N1–C2–C13	112.1 (2)	C3–C2–C13	114.0 (2)
C2–C3–C4	107.3 (2)	C3–C4–C5	115.1 (2)
C3–C4–N12	103.7 (2)	C5–C4–N12	105.6 (2)
C4–C5–C6	103.6 (2)	C5–C6–C7	130.9 (2)
C5–C6–C11	110.0 (2)	C7–C6–C11	119.2 (3)
C6–C7–C8	118.7 (2)	C7–C8–C9	121.5 (3)
C8–C9–C10	120.7 (3)	C9–C10–C11	117.3 (2)
C6–C11–C10	122.7 (3)	C6–C11–N12	111.4 (3)
C10–C11–N12	125.8 (2)	N1–N12–C4	109.5 (2)
N1–N12–C11	114.0 (3)	C4–N12–C11	106.5 (2)
C2–C13–C14	120.9 (3)	C2–C13–C18	119.7 (3)
C14–C13–C18	119.3 (3)	C13–C14–C15	120.1 (3)
C14–C15–C16	119.9 (3)	C15–C16–C17	120.3 (3)
C16–C17–C18	120.9 (3)	C13–C18–C17	119.5 (4)

93.6°.

TABLE IV. Least-Squares Planes and Deviations of Atoms from the Planes

Plane 1: a plane defined by the benzene ring A
$0.2259X-0.7801Y+0.5835Z+4.6338=0$
C6 −0.001; C7 −0.003; C8 0.004; C9 −0.002; C10 −0.002; C11 0.003

Plane 2: a plane defined by the benzene ring A and atoms C4, C5 and N12
$0.2222X-0.7955Y+0.5638Z+4.7183=0$
C4 0.147; C5 −0.052; C6 −0.032; C7 −0.011; C8 0.031; C9 0.035; C10 0.011; C11 −0.017 N12 −0.105

Plane 3: a plane defined by atoms N1, C2, C3, C4, and N12
$-0.6299X-0.7642Y-0.1389Z+8.1878=0$
N1 −0.147; C2 0.100; C3 −0.015; C4 −0.072; N12 0.140

Data Collection and Solution of the Molecular Structure Compound **3** for the X-ray studies was prepared by the synthetic method described previously.[1] The crystal used for the X-ray study was obtained from methanol solution and had dimensions of approximately 0.3 × 0.3 × 0.25 mm. The unit cell parameters at room temperature were refined by the least-squares method using the Bragg angles (CuK_α, $\lambda=1.54178$ Å) of 24 reflections ($30° < 2\theta < 45°$). The crystal data are given in Table I. Intensity data were collected at room temperature on a Rigaku AFC diffractometer with nickel-filtered CuK_α radiation. The θ–2θ scan mode was employed. A total of 1762 unique reflections were measured with $2\theta < 125°$. Lorentz and polarization corrections were applied in the usual manner, but no absorption correction was applied ($\mu = 5.09\,\text{cm}^{-1}$ for CuK_α). Standard deviations in the intensities, $\sigma(F_o)$, were derived directly from counting statistics.

The structure was solved by direct methods using the program MULTAN[3] to calculate the phases of the 300 $|E|$ values with $|E| > 1.43$. Atomic parameters were refined by the block-diagonal least-squares procedure. All of the hydrogen atoms were readily located on the difference Fourier map. In the further refinement, anisotropic and isotropic thermal parameters were applied to the non-hydrogen and hydrogen atoms, respectively. The refinement converged to a conventional $R=(\Sigma||F_o|-|F_c||/\Sigma|F_o|)$ of 0.053 and a weighted $R_w=(\Sigma\omega(|F_o|-|F_c|)^2/\Sigma\omega|F_o|^2)^{1/2}$ of 0.060. Atomic scattering factors were taken from "International Tables for X-Ray Crystallography."[4] Mathematical and computational details are noted elsewhere.[5] Calculations were carried out by using the UNICS program system[6] on an ACOS 850 computer at the Crystallographic Research Center, Institute for Protein Research, Osaka University. The final positional parameters of non-hydrogen atoms with equivalent isotropic temperature factors are given in Table IIa and IIb.

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