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CRYSTAL AND MOLECULAR STRUCTURE OF 2-BENZOLY-5-PHENYLPYRROLE

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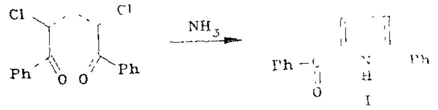
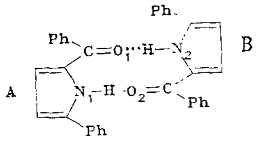
An x-ray diffraction investigation of 2-benzoyl-5-phenylpyrrole, whose molecules are combined as dimers in the crystal, has been carried out. The bond lengths and angles have been presented.

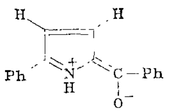
We previously [1] showed that 2,4-dichloro-3R-1,5-pentanediones undergo heterocyclization under the action of ammonia to form the corresponding 3-chloropyridines. The α,α'-dichlorodiketone, which does not have substituent in position 3, reacts with ammonia to form a compound, which is assigned the structure of 2-benzoyl-5-phenylpyrrole (I), according to the data from IR and PMR spectroscopy:



The PMR spectrum of I in $CDCl_3$ shows not only a multiplet for the aromatic protons at δ 7.21-7.97 ppm and a singlet for the >N—H proton at 10.18 ppm, but also signals in the form of two double doublets at 6.62 and 6.93 ppm, which can probably be assigned to the 3-H and 4-H protons of the pyrrole ring. It is difficult to explain the splitting of the signals of the protons indicated on the basis of the structure of phenylpyrrole I, and this prompted us to carry out an x-ray diffraction investigation of I for the purpose of rigorously substantiating its structure.

The x-ray diffraction investigation confirmed the hypothesis that compound I has the structure of 2-benzoyl-5-phenylpyrrole (see Experimental). In addition, in the crystal molecules A and B are joined as dimers by means of N—H...O hydrogen bonds:





II

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TABLE 1. Coordinates of Atoms ($\times 10^4$ and $\times 10^3$ for the H atoms) and Their Isotropic Equivalent* (isotropic for the H atoms) Temperature Factors

Atom	Molecule A				Molecule B			
	x	y	z	B_{iso}^{eq} and B_{iso}, Å²	x	y	z	B_{iso}^{eq} and B_{iso}, Å²
O	2983 (2)	326 (2)	9 122 (2)	4,51 (7)	2463 (2)	9233 (2)	11 062 (2)	5,30 (8)
N	4773 (2)	1777 (2)	10 866 (2)	3,28 (8)	424 (2)	8114 (3)	9 379 (2)	3,50 (8)
$C_{(1)}$	3920 (2)	1493 (3)	9 178 (2)	3,4 (1)	1294 (3)	8300 (3)	11 052 (2)	3,5 (1)
$C_{(2)}$	4848 (3)	2311 (3)	10 073 (2)	3,2 (1)	179 (3)	7734 (3)	10 229 (2)	3,3 (1)
$C_{(3)}$	5832 (3)	3699 (3)	10 369 (2)	4,1 (1)	−1264 (3)	6857 (3)	10 099 (2)	3,7 (1)
$C_{(4)}$	6332 (4)	3975 (3)	11 333 (2)	4,5 (1)	−1870 (3)	6711 (3)	9 177 (2)	3,7 (1)
$C_{(5)}$	5667 (3)	2754 (3)	11 644 (2)	3,4 (1)	806 (3)	7500 (3)	8 728 (2)	3,2 (1)
$C_{(6)}$	4063 (3)	2066 (3)	8 307 (2)	3,2 (1)	1020 (3)	7755 (3)	11 931 (2)	3,3 (1)
$C_{(7)}$	2807 (3)	1803 (3)	7 680 (2)	3,8 (1)	1436 (3)	8738 (3)	11 873 (2)	4,0 (1)
$C_{(8)}$	2891 (4)	2253 (4)	6 853 (2)	5,0 (1)	1247 (3)	8295 (4)	12 706 (2)	4,7 (1)
$C_{(9)}$	4239 (4)	2956 (4)	6 620 (2)	5,2 (1)	654 (4)	6836 (4)	13 591 (2)	4,7 (1)
$C_{(10)}$	5489 (4)	3210 (4)	7 225 (2)	4,6 (1)	254 (3)	5851 (3)	13 661 (2)	4,4 (1)
$C_{(11)}$	5411 (3)	2778 (3)	8 067 (2)	3,8 (1)	426 (3)	6298 (3)	12 829 (2)	3,7 (1)
$C_{(12)}$	5834 (3)	2517 (3)	12 601 (2)	3,3 (1)	−904 (3)	7621 (3)	7 736 (2)	3,1 (1)
$C_{(13)}$	5238 (3)	1171 (3)	12 768 (2)	3,8 (1)	324 (4)	8138 (3)	7 305 (2)	3,9 (1)
$C_{(14)}$	5399 (4)	978 (4)	13 681 (2)	4,4 (1)	180 (4)	8174 (4)	6 354 (2)	4,8 (1)
$C_{(15)}$	6154 (4)	2119 (4)	14 447 (2)	4,6 (1)	−1178 (4)	7719 (4)	5 820 (2)	4,8 (1)
$C_{(16)}$	6765 (4)	3466 (4)	14 297 (2)	5,0 (1)	−2398 (3)	7202 (4)	6 233 (2)	4,7 (1)
$C_{(17)}$	6612 (3)	3659 (3)	13 383 (2)	4,3 (1)	−2272 (3)	7154 (3)	7 178 (2)	3,8 (1)
H_N	427 (3)	111 (3)	1 085 (2)	4,9 (7)	112 (3)	852 (3)	928 (2)	6,3 (9)
$H_{(3)}$	601 (3)	434 (3)	996 (2)	4,9 (7)	−167 (3)	654 (3)	1 062 (2)	4,0 (1)
$H_{(4)}$	700 (3)	482 (3)	1 174 (2)	4,7 (7)	−282 (3)	618 (3)	889 (2)	3,6 (6)
$H_{(7)}$	190 (3)	132 (3)	785 (2)	4,1 (6)	177 (3)	973 (3)	1 286 (2)	4,3 (7)
$H_{(8)}$	209 (3)	205 (3)	642 (2)	4,0 (6)	154 (3)	905 (3)	1 432 (2)	6,8 (8)
$H_{(9)}$	434 (3)	324 (3)	605 (2)	6,3 (8)	52 (3)	652 (3)	1 412 (2)	4,9 (7)
$H_{(10)}$	647 (3)	371 (3)	712 (2)	6,9 (9)	−8 (3)	488 (3)	1 266 (2)	4,6 (6)
$H_{(11)}$	628 (3)	296 (3)	851 (2)	3,9 (6)	21 (3)	564 (3)	1 127 (2)	3,7 (6)
$H_{(13)}$	475 (3)	41 (3)	1 226 (2)	4,5 (7)	122 (2)	844 (3)	767 (2)	3,5 (6)
$H_{(14)}$	500 (3)	4 (3)	1 376 (2)	5,0 (7)	104 (3)	855 (3)	609 (2)	5,4 (7)
$H_{(15)}$	629 (3)	200 (3)	1 508 (2)	5,0 (7)	−126 (3)	770 (3)	517 (2)	4,1 (6)
$H_{(16)}$	726 (4)	422 (4)	1 482 (2)	7,8 (9)	−332 (3)	692 (3)	587 (2)	5,6 (7)
$H_{(17)}$	701 (3)	461 (3)	1 331 (2)	5,4 (7)	−311 (3)	681 (3)	748 (2)	4,7 (7)

$* \; B_{iso}^{eq} = \frac{1}{3}\sum_{i}\sum_{j} B_{ij} a_i^* a_j^* (\mathbf{a}_i \mathbf{a}_j)$.

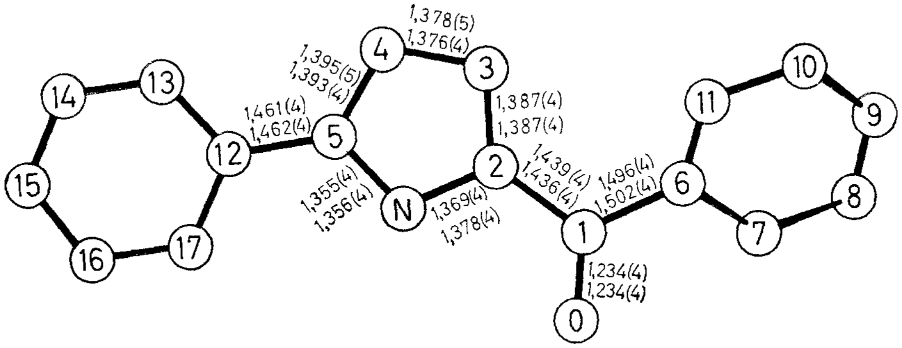

Fig. 1. Geometry of the 2-benzoyl-5-phenylpyrrole molecule.

The parameters of the independent hydrogen bonds are close to the standard values for hydrogen bonds of the N—H...O type [2]: $N_{(1)}...O_{(2)}$ (x, y − 1, z; = 2.940(3), $N_{(1)}$—H = 0.70(3), H...$O_{(2)}$ (x, y − 1, z) = 2.23(3) Å, $\angle N_{(1)}HO_{(2)}$ = 162(2)°, $N_{(2)}...O_{(1)}$(x, 1 + y, z) = 2.094(3), $N_{(2)}$—H = 0.72(3), H...$O_{(1)}$ (x, 1 + y, z) = 2.21(3) Å, $\angle N_{(2)}HO_{(1)}$ = 162(2)°.

The only significant difference between molecules A and B is observed in the rotation of the phenyl rings under the influence of the crystal packing. The plane of the phenyl ring of the benzoyl group forms a dihedral angle equal to 43.8 (in structure A) and 50.0° (in structure B) with the plane of the pyrrole ring. These values are consistent with the data in [3] for a number of 2-aroylpyrroles (whose dihedral angles are equal to 45.5-51.2°) and are governed by the steric repulsion between the $H_{(3)}$ and $H_{(11)}$ atoms, the distance between which with consideration of the departure of the phenyl ring from the plane becomes equal to 2.30 (for A) and 2.48 Å (for B), i.e., is close to twice the van der Waals radius of hydrogen [4]. The same phenyl ring is rotated considerably (37.3 in A and 43.5° in B) relative to the carbonyl group, which is actually coplanar to the pyrrole ring (the dihedral angle equals

TABLE 2. Bond Angles ω in Two Independent Molecules of I

Angle	ω, °	
	Molecule A	Molecule B
$C_{(2)}NH_{(1)}$	121 (3)	125 (3)
$C_{(5)}NH_{(1)}$	127 (3)	125 (3)
$OC_{(1)}C_{(2)}$	120,8 (3)	122,0 (3)
$OC_{(1)}C_{(6)}$	119,1 (3)	119,0 (3)
$NC_{(2)}C_{(1)}$	120,9 (3)	121,0 (3)
$NC_{(2)}C_{(3)}$	106,2 (3)	106,8 (3)
$C_{(2)}C_{(3)}C_{(4)}$	108,0 (3)	107,9 (3)
$C_{(3)}C_{(4)}C_{(5)}$	108,5 (3)	108,3 (3)
$C_{(4)}C_{(5)}N$	106,0 (3)	106,9 (3)
$C_{(4)}C_{(5)}C_{(12)}$	129,3 (3)	128,7 (3)
$NC_{(5)}C_{(12)}$	124,7 (3)	124,3 (3)
$C_{(1)}C_{(6)}C_{(7)}$	118,6 (3)	118,6 (3)
$C_{(1)}C_{(6)}C_{(11)}$	122,8 (3)	122,1 (3)
$C_{(5)}C_{(12)}C_{(13)}$	122,2 (3)	122,6 (3)
$C_{(5)}C_{(12)}C_{(17)}$	120,1 (3)	119,4 (3)
$(CCC)_{Ph}$	117,8—121,1 (4)	118,0—120,6 (4)

6.90 and 7.90° in A and B, respectively). Such rotation weakens the π conjugation of the phenyl ring and the $C{=}O_0$group, as is manifested by the increase in the length of the $C_{(1)}$—$C_{(6)}$ bond to 1.498 (4) Å in comparison to the length of the $C_{(5)}$—$C_{(12)}$ bond [1.461(4) Å]* and the length of a formally single $C_{sp}2$—$C_{sp}2$ bond, for example, in the planar molecule of butadiene (1.465 Å) [4]. The length of the $C_{(1)}$—$C_{(2)}$ bond [1.438(4) Å] is smaller than the length of the $C_{(5)}$—$C_{(12)}$ bond, which is formally a single bond, while the length of the $C_{(1)}{=}O$ bond [1.243(4) Å] is greater than the analogous bond in aldehydes and ketones (1.215 Å) [5]. Such a distribution of the bond lengths is evidence of the significant π-electron delocalization in the N—$C_{(2)}$—$C_{(1)}$—O fragment, which is promoted by the actual coplanarity of the carbonyl group and the pyrrole ring, and suggests a significant contribution for zwitterionic resonance form II [3]. The contribution of canonical form II also accounts for the shortening of the length of the N—$C_{(5)}$ bond [1.356(4) Å] in comparison to the length of the N—$C_{(2)}$ bond [1.374(4) Å] and of the length of the $C_{(3)}$—$C_{(4)}$ bond [1.377(5) Å] in comparison to the analogous bond in the pyrrole molecule (1.417 Å) [4], The lengths of the bonds in both phenyl rings [1.368-1.395(5) Å] are ordinary [5]. As a whole, the distribution of the bond lengths and angles (Table 2) in the molecule of I does not differ from the distributions found in a number of 2-benzoylpyrroles [3].

EXPERIMENTAL

The PMR spectra were recorded in $CDCl_3$ (the internal reference was HMDS) on a Varian Fi-80 spectrometer.

2-Benzoyl-5-phenylpyrrole (I). A solution of 1.4 g (6 mmole) of 1,5-diphenyl-2,4-dichloropentane-1,5-dione in 50 ml of absolute ether is saturated with ammonia for 10 min at 20°C. The reaction mixture is left to stand at room temperature for 7 h, then washed with water, and dried by $CaCl_2$, the solvent is evaporated, and 1.1 g (80%) of phenylpyrrole I with mp 164-165°C (ethanol) are obtained. Found: C, 82.5; H, 5.5; N, 5.6%. Calculated for $C_{17}H_{13}O$: C, 82.4; H, 5.6; N, 5.7%.

The crystals of I are triclinic; at 20°C a = 9.672(1), b = 10.061(1), c = 14.398(2) Å, α = 103.58(1), β = 93.31(2), γ = 107.24(1)°, V = 1288.4(7) Å^3, d_{cal} = 1.280 g/cm^{-3}, z = 4, space group $P\bar{1}$ (two independent molecules A and B).

The unit-cell parameters and the intensities of 2220 independent reflections with $F^2 \geq 3\sigma$ were measured on a Hilger-Watts four-circle automatic diffractometer (λ Mo Kα, graphite monochromator, θ/2θ scan, θ ≤ 30°). The structure of I was solved by the direct method according to the MULTAN program and refined by the full-matrix least-squares method first in the isotropic approximation and then in the anisotropic approximation. The H atoms were placed in calculated positions and included in the refinement in the isotropic approximation. The final R factor was 0.0419 (R_ω = 0.60412). The calculations were carried out on an Eclipse S/200 computer according to the INEXTL programs [6]. The coordinates of the atoms of the two independent molecules A and B are given in Table 1. Some of the angles are given in Table 2.

The geometry of molecule I with some bond lengths (the higher value is for A and the lower for B) is shown in Fig. 1. The bond lengths and angles in the two independent molecules of I actually coincide with the range of the experimental errors (Fig. 1 and Table 2), and the mean values of the geometric parameters for molecules A and B were used in the discussion except in the cases specially noted.

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