CRYSTAL AND MOLECULAR STRUCTURE OF 1,1-BIS(HYDROXYPHENYL)-3-KETOISOINDOLINE

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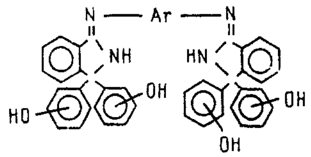
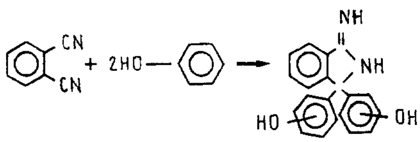
The structure of the condensation product of phthalonitrile and phenol is found by x-ray structure analysis. The structure of a new class of polyheteroarylenes, polhydroxyphenylisoindazenes, is defined using the data obtained.

Earlier we demonstrated [1] that polymers with hydroxyphenyl substituents on the chain, polyhydroxyphenylisoindazenes (PHI) are formed by polycondensation of tetranitriles of tetracarboxylic acids and weakly basic ($pK_a \le 2.7$) diamines in phenol.

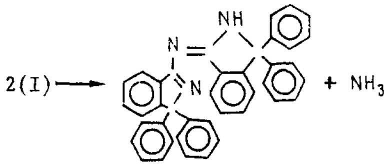


It can be assumed from the literature [2] that the hydroxy groups are located in the 4-position. The model condensation of phthalonitrile with weakly basic diamines in phenol was investigated to define the structure of the PHI. In particular, the first step is condensation of phthalonitrile with phenol.

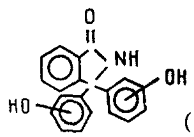


(I)

However, it is very difficult to isolate 1,1-bis(hydroxyphenyl)isoindoline from the reaction mixture since it self-condenses as soon as it forms, according to the scheme



The hydrolysisis of I, 1,1-bis(hydroxyphenyl)-3-ketoisoindoline (II), could be isolated as single crystals by reacting phthalonitrile with phenol containing traces of water. It was identified by x-ray structure analysis (XSA).



(II)

EXPERIMENTAL

1,1-Bis(hydroxyphenyl)-3-ketoisoindoline. A solution of phthalonitrile (0.5 g) in phenol (10 ml) was kept for 10 h at 175°C. A mixture of benzene:petroleum ether (1:1 by volume)

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TABLE 1. Coordinates (×10^4; for H, ×10^3) and Temperature Parameters B_{iso}^{eq} (Å^2) (B_{iso} for H atoms)

Atom	X	Y	Z	B	Atom	X	Y	Z	B
O^1	4084(4)	−6908(4)	5890(1)	4,1(1)	O^{1A}	450(5)	2121(5)	6097(2)	8,1(2)
C^1	4743(6)	−5946(6)	6072(2)	3,5(2)	C^{1A}	−698(7)	1810(7)	5759(2)	5,1(2)
N^2	5036(5)	−4851(4)	5829(1)	3,3(2)	C^{2A}	−863(7)	593(6)	5540(2)	5,5(3)
C^3	5887(6)	−3838(6)	6121(2)	3,4(2)	C^{3A}	−2048(8)	383(7)	5220(2)	6,6(3)
C^4	5972(6)	−4533(5)	6630(2)	3,3(2)	C^{4A}	−3019(7)	1372(8)	5122(2)	6,5(3)
C^5	6556(7)	−4037(6)	7083(2)	4,1(2)	C^{5A}	−2788(7)	2549(8)	5353(2)	6,2(3)
C^6	6499(7)	−4866(7)	7489(2)	5,2(2)	C^{6A}	−1681(7)	2803(7)	5676(2)	5,9(3)
C^7	5857(7)	−6094(7)	7449(2)	5,8(3)					
C^8	5260(7)	−6569(6)	6997(2)	4,8(2)	O^{1B}	1814(6)	803(6)	1623(2)	10,8(2)
C^9	5333(7)	−5752(6)	6592(2)	3,6(2)	C^{1B}	1461(8)	697(8)	2111(2)	7,0(3)
C^{10}	5083(6)	−2529(6)	6127(2)	3,0(2)	C^{2B}	493(8)	1510(9)	2268(3)	8,2(3)
C^{11}	5747(6)	−1322(6)	6098(2)	3,8(2)	C^{3B}	200(9)	1336(10)	2734(3)	10,7(4)
C^{12}	5021(6)	−135(6)	6123(2)	3,8(2)	C^{4B}	847(10)	439(10)	3047(3)	12,2(4)
C^{13}	3660(6)	−185(6)	6183(2)	3,1(2)	C^{5B}	1839(9)	−334(9)	2873(3)	11,1(4)
O^{13}	2904(4)	952(4)	6207(1)	4,4(1)	C^{6B}	2175(9)	−225(8)	2412(3)	8,5(3)
C^{14}	2967(6)	−1361(6)	6216(2)	3,8(2)					
C^{15}	3681(6)	2529(6)	6198(2)	3,5(2)	H^{N^2}	465(5)	−472(4)	551(2)	5,0
C^{16}	7296(6)	−3696(6)	5895(2)	3,5(2)	$H^{O^{13}}$	334(5)	164(5)	616(2)	5,0
C^{17}	7323(6)	−3485(6)	5388(2)	3,6(2)	$H^{O^{17}}$	652(5)	−326(4)	469(2)	5,0
O^{17}	6055(4)	−3419(6)	5098(1)	4,9(2)	$H^{O^{1A}}$	148(5)	125(5)	608(2)	5,0
C^{18}	8537(6)	−3360(7)	5179(2)	4,8(2)	$H^{O^{1B}}$	207(5)	65(5)	159(2)	5,0
C^{19}	9764(7)	−3410(7)	5481(2)	5,7(3)					
C^{20}	9754(7)	−3609(7)	5984(2)	5,6(2)					
C^{21}	8537(6)	−3751(7)	6190(2)	4,4(2)					

TABLE 2. Bond Lengths (Å) and Angles (deg)

Bond	d	Bond	d	Angle	φ	Angle	φ	Angle	φ
$O^{1}–C^{1}$	1,237 (7)	$C^{16}–C^{21}$	1,379 (8)	$O^{1}C^{1}N^{2}$	125,6 (5)	$C^{4}C^{9}C^{8}$	122,3 (6)	$C^{19}C^{20}C^{21}$	120,9
$C^{1}–N^{2}$	1,331 (2)	$C^{17}–O^{17}$	1,392 (7)	$O^{1}C^{1}C^{9}$	128.2 (5)	$C^{3}C^{10}C^{11}$	121,0 (5)	$C^{16}C^{21}C^{20}$	120,1
$C^{1}–C^{9}$	1,477 (8)	$C^{17}–C^{18}$	1,366 (9)	$N^{2}C^{1}C^{9}$	106,2 (5)	$C^{3}C^{10}C^{15}$	120,4 (5)	$C^{1A}O^{1A}H^{O1A}$	112,0
$N^{2}–C^{3}$	1,489 (7)	$O^{17}–H^{O17}$	1,25 (4)	$C^{1}N^{2}C^{3}$	116,2 (5)	$C^{11}C^{10}C^{15}$	118,4 (5)	$O^{1A}C^{1A}C^{2A}$	122,3
$N^{2}–H^{N2}$	0,92 (5)	$C^{18}–C^{19}$	1,377 (9)	$C^{1}N^{2}H^{N2}$	120 (3)	$C^{10}C^{11}C^{12}$	120,8 (5)	$O^{1A}C^{1A}C^{6A}$	115,7
$C^{3}–C^{4}$	1,541 (8)	$C^{19}–C^{20}$	1,377 (9)	$C^{3}N^{2}H^{N2}$	124 (3)	$C^{11}C^{12}C^{13}$	118,7 (5)	$C^{2A}C^{1A}C^{6A}$	122,0
$C^{3}–C^{10}$	1,535 (8)	$C^{20}–C^{21}$	1,367 (9)	$N^{2}C^{3}C^{4}$	98,0 (4)	$C^{12}C^{13}O^{13}$	120,8 (5)	$C^{1A}C^{2A}C^{3A}$	117,5
$C^{3}–C^{16}$	1,561 (8)	$O^{1A}–C^{1A}$	1,405 (8)	$N^{2}C^{3}C^{10}$	109,9 (4)	$C^{12}C^{13}C^{14}$	122,3 (5)	$C^{2A}C^{3A}C^{4A}$	121,3
$C^{4}–C^{5}$	1,391 (8)	$O^{1A}–H^{OA1}$	1,34 (5)	$N^{2}C^{3}C^{16}$	108,5 (4)	$O^{13}C^{13}C^{14}$	116,9 (5)	$C^{3A}C^{4A}C^{5A}$	117,5
$C^{4}–C^{9}$	1,376 (8)	$C^{1A}–C^{2A}$	1,366 (9)	$C^{4}C^{3}C^{10}$	111,2 (5)	$C^{13}O^{13}H^{O13}$	114 (3)	$C^{4A}C^{5A}C^{6A}$	123,7
$C^{5}–C^{6}$	1,388 (8)	$C^{1A}–C^{6A}$	1,386 (9)	$C^{4}C^{3}C^{16}$	115,0 (5)	$C^{13}O^{14}C^{15}$	119,1 (5)	$C^{1A}C^{6A}C^{5A}$	117,6
$C^{6}–C^{7}$	1,387 (9)	$C^{2A}–C^{3A}$	1,39 (1)	$C^{10}C^{3}C^{16}$	113,1 (5)	$C^{10}C^{15}C^{14}$	120,7 (5)	$C^{1B}O^{1B}H^{O1B}$	122,0
$C^{7}–C^{8}$	1,385 (8)	$C^{3A}–C^{4A}$	1,38 (1)	$C^{3}C^{4}C^{5}$	127,2 (5)	$C^{3}C^{16}C^{17}$	120,3 (5)	$O^{1B}C^{1B}C^{2B}$	119,7
$C^{8}–C^{9}$	1,378 (8)	$C^{4A}–C^{5A}$	1,35 (1)	$C^{3}C^{4}C^{9}$	110,9 (5)	$C^{3}C^{16}C^{21}$	121,3 (5)	$O^{1B}C^{1B}C^{6B}$	116,9
$C^{10}–C^{11}$	1,384 (8)	$C^{5A}–C^{6A}$	1,339 (9)	$C^{5}C^{4}C^{9}$	121,9 (5)	$C^{17}C^{16}C^{21}$	118,4 (5)	$C^{2B}C^{1B}C^{6B}$	123,3
$C^{10}–C^{15}$	1,395 (8)	$O^{1B}–C^{1B}$	1,403 (8)	$C^{4}C^{5}C^{6}$	115,9 (5)	$C^{16}C^{17}O^{17}$	117,3 (6)	$C^{1B}C^{2B}C^{3B}$	116,2
$C^{11}–C^{12}$	1,394 (8)	$O^{1B}–H^{O1B}$	0,31 (5)	$C^{5}C^{6}C^{7}$	121,9 (6)	$C^{16}C^{17}C^{18}$	121,8 (5)	$C^{2B}C^{3B}C^{4B}$	123,5
$C^{12}–C^{13}$	1,349 (8)	$C^{1B}–C^{2B}$	1,35 (1)	$C^{6}C^{7}C^{8}$	121,6 (6)	$O^{17}C^{17}C^{18}$	121,0 (5)	$C^{3B}C^{4B}C^{5B}$	117,9
$C^{13}–O^{13}$	1,367 (7)	$C^{1B}–C^{6B}$	1,38 (1)	$C^{7}C^{8}C^{9}$	116,4 (6)	$C^{17}O^{17}H^{O17}$	97 (2)	$C^{4B}C^{5B}C^{6B}$	121,9
$C^{13}–C^{14}$	1,372 (8)	$C^{2B}–C^{3B}$	1,33 (1)	$C^{1}C^{9}C^{4}$	108,5 (5)	$C^{17}C^{18}C^{19}$	118,9 (6)	$C^{1B}C^{6B}C^{5B}$	117,2
$O^{13}–H^{O13}$	0,83 (5)	$C^{3B}–C^{4B}$	1,35 (1)	$C^{1}C^{9}C^{8}$	129,2 (5)	$C^{18}C^{19}C^{20}$	120,0 (6)		
$C^{14}–C^{15}$	1,370 (9)	$C^{4B}–C^{5B}$	1,36 (1)						
$C^{16}–C^{17}$	1,391 (7)	$C^{5B}–C^{6B}$	1,33 (1)						

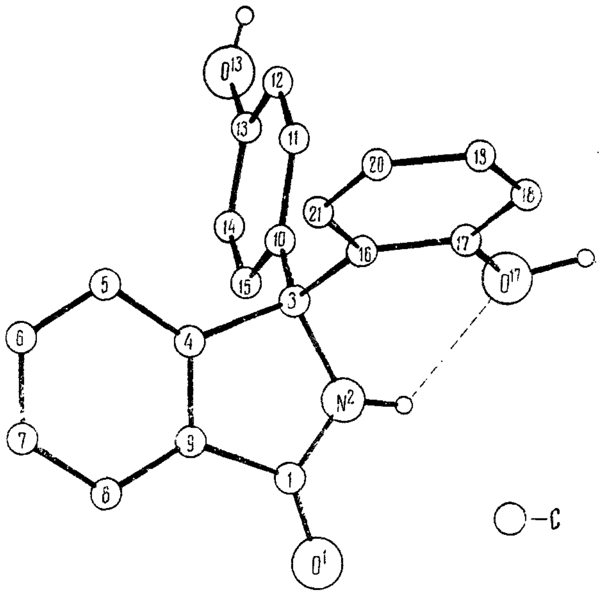


Fig. 1. Structure of II. The intramolecular H-bond is shown by a dashed line.

was then added. The precipitate was filtered off. Crystals of II were separated from the blue precipitate.

The crystals are monoclinic, space group $P2_1/c$, a = 9.717(1), b = 10.084(1), c = 27.066(1) Å, β = 95.82(1)°, Z = 4 ($II \cdot 2C_6H_6O$), V = 2638.4(8) Å³, d_{calc} = 1.279 $g \cdot cm^{-3}$. The unit-cell constants and intensities of reflections were measured on a Hilger-Watts Y-290 automatic four-circle diffractometer (λ Mo Kα, graphite monochromator, θ/2θ-scanning, θ_{max} = 27°). The structure was solved by direct methods (MULTAN programs) and refined by block-diagonal anisotropic least squares (LS) for the nonhydrogen atoms. The H atoms in the benzene rings were assigned geometrically. Their positions were not refined but were readjusted after each LS cycle and included in the calculation of F_{calc} with B_{iso} = 5.0 Å². The H atoms of hydroxyl and imino groups were found in a difference Fourier synthesis and were included in the LS refinement with fixed B_{iso} = 5.0 Å². The final R = 0.042 and R_w = 0.031 for 1184 unique reflections with I ≥ 2σ.

All calculations were performed on an Eclipse S/200 computer using INEXTL programs [3]. The atomic coordinates are given in Table 1; geometric parameters, in Table 2. The molecular structure of II is shown in Fig. 1.

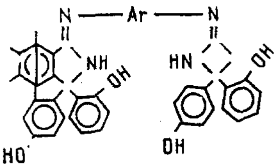
RESULTS AND DISCUSSION

The x-ray structure investigation found that II is 1-(4-hydroxyphenyl)-1-(2-hydroxyphenyl)-3-ketoisoindoline, which crystallizes as the molecular complex with phenol (1:2).

The bond lengths and angles in II (Table 2) are close to their usual values [4]. The bicyclic isoindoline backbone is in fact planar. The deviations of its atoms from the least-squares plane are less than 0.047(6) Å. The observed orientation of the 2-hydroxyphenyl substituent, which is characterized by torsion angles C^4—C^3—C^{16}—C^{17} 159.7(8)°, is controlled by the formation of an intramolecular H-bond N^2—H^{N^2}...O^{17} [N...O 2.716(6), H...O 2.27(5) Å, angle N—H...O 110(4)°]. The other 4-hydroxyphenyl substituent is oriented perpendicular to the neighboring aromatic systems. It forms dihedral angles 86.2° with the isoindoline fragment and 81.6° with the 2-hydroxyphenyl group. Apparently this minimizes intramolecular steric hindrances.

A chain along the Y axis in the crystal of II is formed by intermolecular H-bonds O^{13}—$H^{O^{13}}$...$O^{1'}$ [O...O 2.628(6), H...O 1.81(5) Å, angle O—H...O 166(4)°] that are joined pairwise by H-bonds O^{17}—$H^{O^{17}}$...O1" [O...O 2.686(6) Å, H...O 1.63(5) Å, angle O—H...O 138(5)°]. Phenol molecules are bonded to each other [O^{1A}...O^{1B} 2.790(7) Å] and to O^{13} of the hydroxyl group of II [O^{1A}...O^{13} 2.650(6) Å], forming double chains of II. A six-membered heterocycle is formed by H-bond H^{N^2}...O^{17} and not N^2...$H^{O^{17}}$. This indicates that the unshared electron pair of N^2 is conjugated in the isoindoline.

The results obtained enabled the structure of the polycondensation products of tetranitriles of tetracarboxylic acids and weakly basic diamines to be defined. The PHI are thought to have the structure



We have found that the luminescence quantum yield of a solution of PHI based on pyromellitonitrile and 2,7-dimethyl-3,6-diaminoacridine is 50%, i.e., it seems anomalously high for a polymer with flexible side groups. The data obtained in the present work suggest that the reason for the high luminescence quantum yield is the decrease of intramolecular flexibility in the polymeric chain owing to formation of intramolecular H-bonds and the limited flexibility of the hydroxyphenyl side groups.

The presence of hydroxy groups in the o-position enables the PHI to be viewed as macromolecular ligands and makes them promising as starting materials for synthesizing macromolecular metal complexes.

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