Chemistry of Heterocyclic Compounds, Vol. 41, No. 6, 2005

SYNTHESIS, STRUCTURE, AND BIOLOGICAL ACTIVITY OF [2.2]PARACYCLOPHANE DERIVATIVES. 8*. α-PYRIDYL([2.2]PARACYCLOPHAN-4-YL)-PHENYLMETHANOL: STRUCTURE OF THE COMPLEX WITH Cu(II) CHLORIDE AND INTRAMOLECULAR CYCLIZATION

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The reaction of 2-benzoylpyridine with 4-([2.2]paracyclophanyl)lithium or of 4-benzoyl[2.2]paracyclophane with 2-pyridyllithium gave α-pyridyl([2.2]paracyclophan-4-yl)phenylmethanol. X-ray analysis has been used to study the molecular and crystalline structure of its complex with Cu(II) chloride. It was found that this triaryl-substituted methanol undergoes an intramolecular cyclocondensation in refluxing formic acid and involves the pyridine ring and the cyclophane substituent. Heterocyclization at the ortho-position of the latter gives 10-phenyl[2.2]paracyclophano[4,5-b]indolizine and cyclization at the pseudo-gem-position the 1-phenyl-1,1a-dehydro-6-aza[3.2.2](1,2,5)-6H-cyclophano[1,2-a]pyridine. The compounds prepared have luminescent properties.

Keywords: α-pyridyl([2.2]paracyclophan-4-yl)phenylmethanol, [2.2]paracyclophano[4,5-*b*]indolizine, 1-phenyl-1,1a-dehydro-6-aza[3.2.2](1,2,5)-6H-cyclophano[1,2-*a*]pyridine, complex with Cu(II) chloride, heterocyclization, luminescent properties.

It is known that the main acid catalyzed reaction of 1-(paracyclophan-4-yl)-1-(α-pyridyl)ethanol is dehydration to the corresponding 1,1-diarylethylene and cyclocondensation at the *ortho*-position of the paracyclophane to form a paracyclophano[4,5-*b*]indolizine [2]. The product of a transannular type heterocyclization (at the *pseudo*-*gem*-position of the paracyclophane) could not be prepared in a pure state due to the low chemoselectivity of this complex reaction.

In going from the studied disubstituted ethanol to a triaryl-substituted methanol one of the indicated routes for the reaction not realized is the dehydration to form an alkene. This leads one to expect an increased yield of a product of transannular cyclization and markedly enough to permit a successful separation from the reaction mixture. With this in view we have synthesized α-pyridyl([2.2]paracyclophan-4-yl)phenylmethanol (**2**)

* For Communication 7 see [1].

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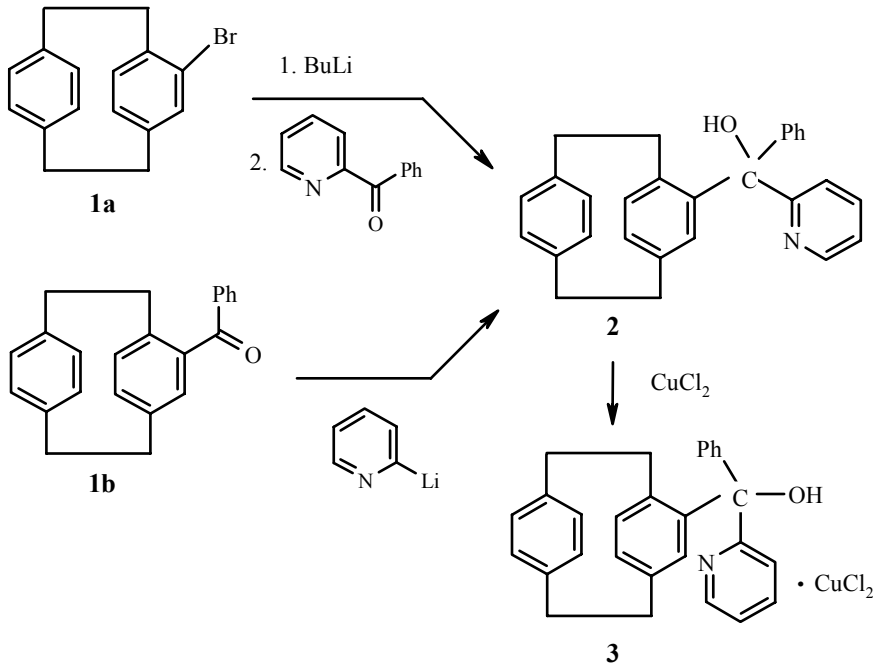
starting from 2-benzoylpyridine and 4-([2.2]paracyclophanyl)lithium (which was prepared from the 4-bromo derivative **1a**) or from 2-pyridyllithium and 4-benzoyl[2.2]paracyclophane (**1b**) in respective yields of 8 and 62%.



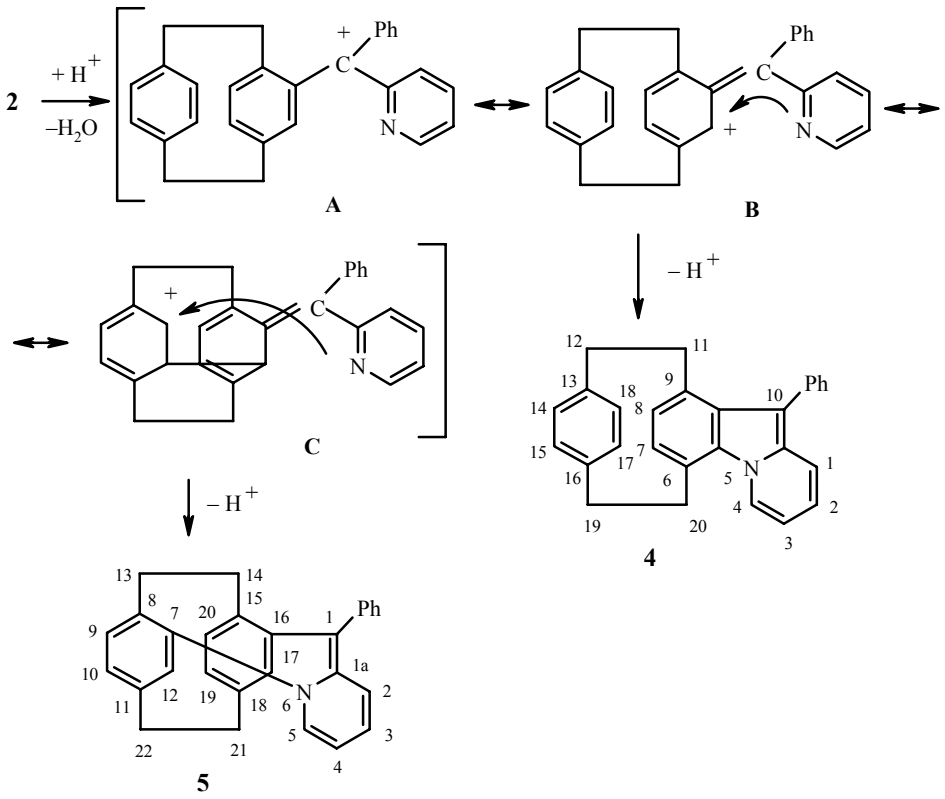
The structure of this triaryl substituted methanol **2** was confirmed from spectroscopic data (see Experimental) and by X-ray analysis of its complex with Cu(II) chloride **3**.

Fig. 1 shows that the complex occurs as a dimer structure which is realized in the crystal *via* pentacoordinate Cu(II) ions. X-ray analysis has shown that compound **3** is a centrosymmetric dimer linked by two asymmetric μ^2-bridging chlorine atoms [bond lengths Cu(1)–Cl(2) 2.585(2) and Cu(1)–Cl(2a) 2.261(2) Å]. The copper atom is pentacoordinated and can be represented either as a distorted trigonal bipyramid (3+2) with the Cl(1), Cl(2), and O(1) atoms in an equatorial position and the Cl(2a) and N(1) atoms in an axial position or as a distorted tetragonal pyramid (4+1) with the Cl(1), Cl(2a), O(1), and N(1) atoms in the base of pyramid and the Cl(2) atom at its apex.

The tetrahedral geometry of the central C(1) atom is slightly distorted (the range of values of the valence angles being 104.7(5) to 113.7(5)°), very likely as a result of steric effects. The paracyclophane substituent has the usual structure [3]. The dimers form stable associates (Fig. 1) with two molecules of ethanol *via* strong hydrogen bonds (O(1)–H(1o)···O(1s)–O(1)···O(1s) 2.627(7), H(1o)···O(1s) 2.01(6) Å, angle O(1)–H(1o)···O(1s) 169(5)° and O(1s)–H(1os)···Cl(1a)–O(1s)···Cl(1a) 3.168(6), H(1os)···Cl(1a) 2.39(5) Å, angle O(1)–H(1o)···O(1s) 163(5)°) and these form the crystals of compound **3** (Fig. 2). The associates in the crystal are spaced at van der Waal distances.

According to the ^{1}H NMR data for methanol **2** it is formed as two diastereomers (mp 123-126°C) in the ratio 1:1. This is indicated by the presence of two signals (at 8.7 and 8.5 ppm) for the H-α of the pyridine ring and also by two signals for the OH groups (at 8.5 and 5.5 ppm) with integrated intensities of 0.5 H each.

The cyclocondensation of the alcohol **2** was carried out by refluxing in formic acid for 2 h. According to TLC the reaction mixture consists of two substances with close chromatographic mobilities. Column chromatography on alumina and elution with hexane gave the two pure products as the cyclophanoindolizine **4** (which is apparently formed *via* the cations **A** and **B**) and the azacyclophanopyridine **5** formed through an intramolecular nucleophilic transannular attack in the cation **C**.



Both substances **4** and **5** were obtained as high-melting, bright-yellow crystals with mp 174-175 and 218-221°C and yields of 25 and 35% respectively. The structure of the isomeric compounds **4** and **5** was confirmed mainly on the basis of an analysis of their UV spectra. Hence the less high-melting substance **4**

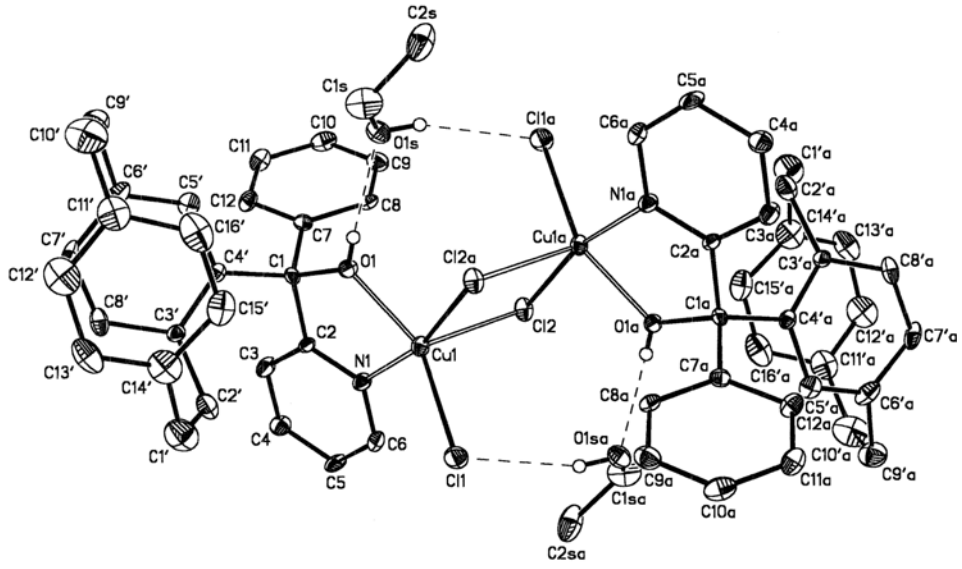


Fig. 1. Molecular structure of compound **3** with 30% ellipsoids of anisotropic displacement (hydrogen bonds shown by dashed lines).

TABLE 1. Coordinates ($\times 10^4$) and Equivalent Thermal Parameters ($\times 10^3$) for Non-hydrogen Atoms in Compound **3**

Atom	*x*	*y*	*z*	U_{eq}, Å^2
Cu(1)	874(1)	764(1)	-3(1)	21(1)
Cl(1)	1642(1)	238(1)	729(1)	32(1)
Cl(2)	-660(1)	729(1)	378(1)	25(1)
O(1)	761(3)	1333(3)	-761(2)	22(1)
N(1)	1028(3)	2190(3)	151(3)	21(2)
C(1)	886(3)	2362(4)	-859(3)	17(2)
C(2)	1046(3)	2791(4)	-283(3)	17(2)
C(3)	1190(4)	3789(4)	-212(3)	27(2)
C(4)	1325(4)	4152(4)	309(3)	28(2)
C(5)	1304(4)	3531(4)	763(3)	26(2)
C(6)	1156(4)	2555(5)	671(4)	28(2)
C(7)	54(3)	2829(4)	-1061(3)	19(2)
C(8)	-720(4)	2482(4)	-874(3)	24(2)
C(9)	-1467(4)	2937(5)	-1018(3)	31(2)
C(10)	-1452(4)	3757(5)	-1348(3)	32(2)
C(11)	-689(4)	4131(4)	-1531(3)	28(2)
C(12)	71(4)	3671(4)	-1388(3)	25(2)
C(1')	3643(5)	1676(6)	-624(4)	55(3)
C(2')	2845(4)	2369(5)	-538(3)	34(2)
C(3')	2465(4)	2685(4)	-1084(3)	19(2)
C(4')	1629(3)	2514(4)	-1257(3)	18(2)
C(5')	1481(4)	2376(4)	-1830(3)	26(2)
C(6')	2110(4)	2498(5)	-2218(3)	32(2)
C(7')	2849(4)	2963(4)	-2050(4)	30(2)
C(8')	3020(4)	3036(4)	-1498(4)	29(2)
C(9')	2073(5)	1988(6)	-2788(4)	45(2)
C(10')	2708(6)	1084(7)	-2818(4)	66(3)
C(11')	3105(5)	846(5)	-2291(4)	44(2)
C(12')	3901(5)	1160(5)	-2143(4)	52(3)
C(13')	4148(4)	1301(5)	-1577(4)	46(3)
C(14')	3571(5)	1113(5)	-1174(4)	46(2)
C(15')	2852(5)	566(4)	-1305(4)	40(2)
C(16')	2619(5)	451(5)	-1856(5)	52(3)
O(1s)	-185(3)	513(3)	-1533(2)	30(1)
C(1s)	218(5)	-205(6)	-1862(4)	53(2)
C(2s)	-372(6)	-1017(5)	-2037(4)	57(3)

showed several absorption band maxima in the long wavelength region typical of similar benzoindolizine systems (λ_{max} 420, 430, 440 and 480 nm) [4, 5]. The UV spectrum of the transannular cyclization product **5** showed only one band (420 nm) in this region.

The ^{1}H NMR spectrum of the cyclophanoindolizine **4** showed dehydropyridine fragment protons at 6.60 (H-3) and 6.90 (H-2) as multiplets and at 7.40 (H-1) and 8.45 ppm (H-4) as doublets with J = 7.8 and 7.7 Hz respectively. The six aromatic protons of the paracyclophane fragment give four doublet signals each with an integrated intensity of one proton each (with J = 8.1-8.3 Hz) and one broadened signal of two proton units, the half height width ($J_{1/2}$) of which is 6.7 Hz and thus suggests the presence of one tetrasubstituted and one *para*-substituted benzene ring in the **4** molecule. In the ^{1}H NMR spectrum of the transannular cyclization product **5** the two aromatic protons H-17 and H-12 in the paracyclophane ring appeared as two narrow singlets at 6.08 and 7.10 ppm respectively with proton H-12 1.02 ppm to lower field due to the deshielding effect of the nitrogen atom. The remaining four protons of this fragment showed one broadened signal at 6.70 ppm with $J_{1/2}$ = 7.0 Hz rather than the expected doublet signals.

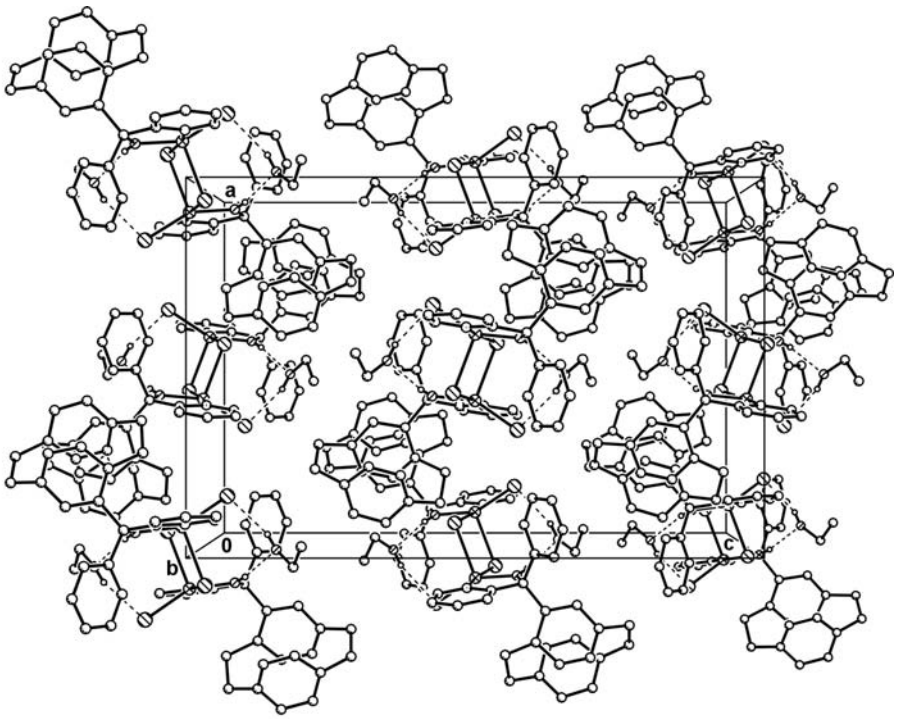


Fig. 2. Crystal packing of the H-bonded associates **3** along the Y axis (hydrogen bonds shown by dashed lines).

TABLE 2. Bond Lengths (*d*) in Compound **3**

Bond	*d*, Å	Bond	*d*, Å
Cu(1)–O(1)	1.980(6)	C(11)–C(12)	1.397(8)
Cu(1)–N(1)	2.005(5)	C(1')–C(14')	1.529(12)
Cu(1)–Cl(1)	2.2489(19)	C(1')–C(2')	1.589(9)
Cu(1)–Cl(2)#1	2.2613(15)	C(2')–C(3')	1.502(9)
Cu(1)–Cl(2)	2.5851(16)	C(3')–C(4')	1.401(8)
Cl(2)–Cu(1)#1	2.2613(15)	C(3')–C(8')	1.406(9)
O(1)–C(1)	1.445(6)	C(4')–C(5')	1.402(9)
N(1)–C(2)	1.327(8)	C(5')–C(6')	1.369(9)
N(1)–C(6)	1.357(8)	C(6')–C(7')	1.387(9)
C(1)–C(2)	1.520(9)	C(6')–C(9')	1.534(11)
C(1)–C(4')	1.524(8)	C(7')–C(8')	1.353(10)
C(1)–C(7)	1.537(7)	C(9')–C(10')	1.594(10)
C(2)–C(3)	1.398(7)	C(10')–C(11')	1.445(12)
C(3)–C(4)	1.359(9)	C(11')–C(12')	1.372(11)
C(4)–C(5)	1.381(9)	C(11')–C(16')	1.402(11)
C(5)–C(6)	1.376(8)	C(12')–C(13')	1.422(12)
C(7)–C(8)	1.384(8)	C(13')–C(14')	1.352(11)
C(7)–C(12)	1.396(8)	C(14')–C(15')	1.395(10)
C(8)–C(9)	1.375(8)	C(15')–C(16')	1.376(11)
C(9)–C(10)	1.376(9)	O(1s)–C(1s)	1.410(9)
C(10)–C(11)	1.378(9)	C(1s)–C(2s)	1.511(11)

The mass spectrometric behavior of compounds **4** and **5** also supported their structure. The cyclophanoindolizine **4** was of low stability under electron impact conditions. Its molecular ion peak M^+ (*m/z* 373) has a low intensity (20%) and readily loses a *para*-xylylene fragment (*m/z* 104) to give the $[M-104]^+$ ion with *m/z* 269 and this has maximum intensity. In compound **5**, in which both benzene nuclei of the paracyclophane part are, in fact, bonded by three bridges, the maximum intensity peak is that of the molecular ion M^+.

A study of the luminescent properties of compounds **2, 4** and **5** has shown that they show strong fluorescence with λ_{max} 358 (alcohol **2**), 408 and 528 (cyclophanoindolizine **4**), and 396 nm (azacyclophanopyridine **5**). The appearance in compound **4** of a second fluorescence peak (at 528 nm) confirms the formation of the benzoindolizine fragment since the presence of a similar band is typical of the benzoindolizine structure [6]. The absence of a similar fluorescence band in the spectrum of compound **5** points to the formation of another structural framework in which the π-conjugation between the cyclophane and pyridine fragments is disturbed as a result of orthogonality (a transannular cyclization effect). Hence the fluorescence spectra can also serve to establish the structure of the paracyclophane-containing products of the type discussed. They appear promising as potential luminophores [7].

TABLE 3. Valence Angles (ω) in Compound **3**

Angle	ω, deg.	Angle	ω, deg.
O(1)–Cu(1)–N(1)	78.2(2)	Cl(2)#1–Cu(1)–Cl(2)	89.05(5)
O(1)–Cu(1)–Cl(1)	152.62(15)	Cu(1)#1–Cl(2)–Cu(1)	90.95(5)
N(1)–Cu(1)–Cl(1)	95.95(17)	C(1)–O(1)–Cu(1)	121.4(4)
O(1)–Cu(1)–Cl(2)#1	88.91(14)	C(2)–N(1)–C(6)	119.0(5)
N(1)–Cu(1)–Cl(2)#1	167.11(18)	C(2)–N(1)–Cu(1)	117.7(5)
Cl(1)–Cu(1)–Cl(2)#1	95.65(6)	C(6)–N(1)–Cu(1)	123.2(4)
O(1)–Cu(1)–Cl(2)	104.23(14)	O(1)–C(1)–C(2)	104.7(5)
N(1)–Cu(1)–Cl(2)	93.82(14)	O(1)–C(1)–C(4')	109.9(5)
Cl(1)–Cu(1)–Cl(2)	102.84(7)	C(2)–C(1)–C(4')	112.7(5)
O(1)–C(1)–C(7)	110.0(4)	C(3')–C(4')–C(5')	117.9(6)
C(2)–C(1)–C(7)	105.4(5)	C(3')–C(4')–C(1)	124.1(6)
C(4')–C(1)–C(7)	113.7(5)	C(5')–C(4')–C(1)	117.7(5)
N(1)–C(2)–C(3)	121.2(6)	C(6')–C(5')–C(4')	121.8(6)
N(1)–C(2)–C(1)	117.8(5)	C(5')–C(6')–C(7')	117.9(7)
C(3)–C(2)–C(1)	121.0(6)	C(5')–C(6')–C(9')	121.3(7)
C(4)–C(3)–C(2)	119.7(6)	C(7')–C(6')–C(9')	120.0(6)
C(3)–C(4)–C(5)	119.5(6)	C(8')–C(7')–C(6')	119.0(6)
C(6)–C(5)–C(4)	118.6(7)	C(7')–C(8')–C(3')	122.5(6)
N(1)–C(6)–C(5)	122.1(7)	C(6')–C(9')–C(10')	111.7(7)
C(8)–C(7)–C(12)	118.8(5)	C(11')–C(10')–C(9')	114.2(7)
C(8)–C(7)–C(1)	120.5(5)	C(12')–C(11')–C(16')	115.5(9)
C(12)–C(7)–C(1)	120.3(5)	C(12')–C(11')–C(10')	123.3(9)
C(9)–C(8)–C(7)	121.2(6)	C(16')–C(11')–C(10')	119.9(8)
C(8)–C(9)–C(10)	120.0(6)	C(11')–C(12')–C(13')	122.5(8)
C(9)–C(10)–C(11)	120.2(6)	C(14')–C(13')–C(12')	118.0(8)
C(10)–C(11)–C(12)	120.1(6)	C(13')–C(14')–C(15')	119.2(9)
C(7)–C(12)–C(11)	119.7(5)	C(13')–C(14')–C(1')	117.9(8)
C(14')–C(1')–C(2')	110.8(6)	C(15')–C(14')–C(1')	121.7(8)
C(3')–C(2')–C(1')	112.0(6)	C(16')–C(15')–C(14')	119.7(8)
C(4')–C(3')–C(8')	115.8(6)	C(15')–C(16')–C(11')	121.3(8)
C(4')–C(3')–C(2')	125.8(6)	O(1s)–C(1s)–C(2s)	113.1(7)
C(8')–C(3')–C(2')	117.6(6)		

TABLE 4. Torsional angles (τ) in Compound **3**

Angle	τ, deg.	Angle	τ, deg.
O(1)–Cu(1)–Cl(2)–Cu(1)#1	88.63(15)	C(8)–C(9)–C(10)–C(11)	-0.7(11)
N(1)–Cu(1)–Cl(2)–Cu(1)#1	167.42(18)	C(9)–C(10)–C(11)–C(12)	0.8(11)
Cl(1)–Cu(1)–Cl(2)–Cu(1)#1	-95.58(7)	C(8)–C(7)–C(12)–C(11)	-1.6(10)
Cl(2)#1–Cu(1)–Cl(2)–Cu(1)#1	0.0	C(1)–C(7)–C(12)–C(11)	-174.9(6)
N(1)–Cu(1)–O(1)–C(1)	4.2(4)	C(10)–C(11)–C(12)–C(7)	0.4(10)
Cl(1)–Cu(1)–O(1)–C(1)	-75.8(5)	C(14')–C(1')–C(2')–C(3')	-28.0(8)
Cl(2)#1–Cu(1)–O(1)–C(1)	-176.0(4)	C(1')–C(2')–C(3')–C(4')	120.9(7)
Cl(2)–Cu(1)–O(1)–C(1)	95.2(4)	C(1')–C(2')–C(3')–C(8')	-47.7(7)
O(1)–Cu(1)–N(1)–C(2)	-4.5(4)	C(8')–C(3')–C(4')–C(5')	21.4(7)
Cl(1)–Cu(1)–N(1)–C(2)	148.4(4)	C(2')–C(3')–C(4')–C(5')	-147.3(6)
Cl(2)#1–Cu(1)–N(1)–C(2)	-5.7(9)	C(8')–C(3')–C(4')–C(1)	-165.3(5)
Cl(2)–Cu(1)–N(1)–C(2)	-108.3(4)	C(2')–C(3')–C(4')–C(1)	25.9(9)
O(1)–Cu(1)–N(1)–C(6)	178.9(5)	O(1)–C(1)–C(4')–C(3')	-93.9(6)
Cl(1)–Cu(1)–N(1)–C(6)	-28.2(5)	C(2)–C(1)–C(4')–C(3')	22.4(7)
Cl(2)#1–Cu(1)–N(1)–C(6)	177.7(4)	C(7)–C(1)–C(4')–C(3')	142.3(5)
Cl(2)–Cu(1)–N(1)–C(6)	75.1(4)	O(1)–C(1)–C(4')–C(5')	79.4(6)
Cu(1)–O(1)–C(1)–C(2)	-3.1(5)	C(2)–C(1)–C(4')–C(5')	-164.3(5)
Cu(1)–O(1)–C(1)–C(4')	118.2(5)	C(7)–C(1)–C(4')–C(5')	-44.4(7)
Cu(1)–O(1)–C(1)–C(7)	-115.9(5)	C(3')–C(4')–C(5')–C(6')	-6.5(8)
C(6)–N(1)–C(2)–C(3)	-0.3(8)	C(1)–C(4')–C(5')–C(6')	179.9(5)
Cu(1)–N(1)–C(2)–C(3)	-177.1(4)	C(4')–C(5')–C(6')–C(7')	-13.6(9)
C(6)–N(1)–C(2)–C(1)	-178.9(5)	C(4')–C(5')–C(6')–C(9')	155.9(6)
Cu(1)–N(1)–C(2)–C(1)	4.3(6)	C(5')–C(6')–C(7')–C(8')	17.9(9)
O(1)–C(1)–C(2)–N(1)	-0.9(6)	C(9')–C(6')–C(7')–C(8')	-151.8(6)
C(4')–C(1)–C(2)–N(1)	-120.2(5)	C(6')–C(7')–C(8')–C(3')	-2.1(9)
C(7)–C(1)–C(2)–N(1)	115.2(5)	C(4')–C(3')–C(8')–C(7')	-17.7(8)
O(1)–C(1)–C(2)–C(3)	-179.5(5)	C(2')–C(3')–C(8')–C(7')	152.0(6)
C(4')–C(1)–C(2)–C(3)	61.1(7)	C(5')–C(6')–C(9')–C(10')	-104.4(8)
C(7)–C(1)–C(2)–C(3)	-63.4(6)	C(7')–C(6')–C(9')–C(10')	64.9(9)
N(1)–C(2)–C(3)–C(4)	0.8(9)	C(6')–C(9')–C(10')–C(11')	7.6(10)
C(1)–C(2)–C(3)–C(4)	179.4(5)	C(9')–C(10')–C(11')–C(12')	-97.0(9)
C(2)–C(3)–C(4)–C(5)	-1.1(9)	C(9')–C(10')–C(11')–C(16')	69.3(10)
C(3)–C(4)–C(5)–C(6)	0.7(9)	C(16')–C(11')–C(12')–C(13')	-14.7(10)
C(2)–N(1)–C(6)–C(5)	0.0(9)	C(10')–C(11')–C(12')–C(13')	152.2(7)
Cu(1)–N(1)–C(6)–C(5)	176.6(5)	C(11')–C(12')–C(13')–C(14')	0.1(10)
C(4)–C(5)–C(6)–N(1)	-0.2(9)	C(12')–C(13')–C(14')–C(15')	16.2(9)
O(1)–C(1)–C(7)–C(8)	32.6(8)	C(12')–C(13')–C(14')–C(1')	-151.8(7)
C(2)–C(1)–C(7)–C(8)	-79.8(6)	C(2')–C(1')–C(14')–C(13')	114.7(7)
C(4')–C(1)–C(7)–C(8)	156.3(6)	C(2')–C(1')–C(14')–C(15')	-53.0(9)
O(1)–C(1)–C(7)–C(12)	-154.2(6)	C(13')–C(14')–C(15')–C(16')	-17.5(9)
C(2)–C(1)–C(7)–C(12)	93.5(7)	C(1')–C(14')–C(15')–C(16')	150.0(7)
C(4')–C(1)–C(7)–C(12)	-30.5(8)	C(14')–C(15')–C(16')–C(11')	2.1(9)
C(12)–C(7)–C(8)–C(9)	1.7(10)	C(12')–C(11')–C(16')–C(15')	13.4(9)
C(1)–C(7)–C(8)–C(9)	175.0(6)	C(10')–C(11')–C(16')–C(15')	-154.0(7)
C(7)–C(8)–C(9)–C(10)	-0.6(10)		

EXPERIMENTAL

^{1}H NMR spectra were recorded on a Bruker AM-300 (300 MHz) instrument using $CDCl_3$ and TMS internal standard. IR spectra were taken on a Specord IR-75 instrument for KBr tablets. UV spectra were obtained on a Specord M-40 spectrometer using ethanol. Excitation and fluorescence spectra were recorded on a

Shimadzu RF-540 spectrofluorometer using hexane. Mass spectra were taken on an MX-1303 instrument with an ionization energy of 70 eV. Monitoring of the reaction course and the homogeneity of the obtained compounds was performed using TLC on Silufol UV-254 plates in the solvent system hexane–ethyl acetate (3:1).

X-ray Analysis of Compound 3. Crystals of compound **3** ($C_{56}H_{40}Cl_4Cu_2N_2O_2 \cdot 2C_2H_5OH$, M = 1144.00) are rhombic with space group *Pbca*, at T = 163 K: a = 15.763(3), b = 13.718(3), c = 23.921(5) Å; V = 5172.7(18) Å^3; Z = 4; d_{calc} = 1.469 mg/cm^3; $F(000)$ = 2376; μ = 1.08 mm^{-1}. Unit cell parameters and the intensities of 4551 reflections were measured on a Syntex $P2_1$ four circle, automatic diffractometer (T = 163 K, λMoKα radiation, graphite monochromator, $\theta/2\theta$ scanning, θ_{max} = 28°). The structure was solved by a direct method and refined in a full matrix least squares analysis in the anisotropic approximation for non-hydrogen atoms. The ethanol solvate molecule was revealed in difference Fourier synthesis. The hydrogen atoms of the hydroxyl groups were localized directly by difference Fourier synthesis and refined in the isotropic approximation. The positions of the remaining hydrogen atoms were calculated geometrically and refined in the isotropic approximation with fixed positions (the "riding" model) and thermal parameters [U_{iso}(H) = 1.5 U_{eq}(C) for CH_3 groups and U_{iso}(H) = 1.2 U_{eq}(C) for all of the remaining groups]. The final difference factors were R_1 = 0.074 for 3292 independent reflections with $I > 2\sigma(I)$ and wR_2 = 0.1592 for all 4551 independent reflections. All of the calculations were carried out using the SHELXTL PLUS (version 5.10) computer package [8]. Tables 1-3 show the data for the atomic coordinates, bond lengths, valence and torsional angles, and anisotropic thermal parameters for compound **3**.

α-Pyridyl([2.2]paracyclophan-4-yl)phenylmethanol (2). A. A solution of 2-benzoylpyridine (2.56 g, 14 mmol) in benzene (5 ml) was added to a benzene solution of 4-([2.2]paracyclophanyl)lithium prepared from butyllithium (17 mmol) and 4-bromoparacyclophane (**1a**) (4 g, 14 mmol) and the mixture was heated with stirring for 6 h. After cooling, the reaction mixture was treated with a saturated solution of ammonium chloride. The organic layer was separated and the aqueous layer was extracted with ether (3 × 50 ml). The combined extracts were dried over $MgSO_4$. Ether was evaporated and compound **2** was separated chromatographically on an alumina column using hexane–ethyl acetate eluent (30:1). Yield 0.44 g (8%).

B. 4-Benzoyl[2.2]paracyclophane (**1b**) (4 g, 13 mmol) was added to a solution of 2-pyridyllithium in absolute ether (50 ml) prepared from butyllithium (26 mmol) and 2-bromopyridine (1.3 ml, 13 mmol) at -80°C and the mixture was stirred at -40 to -30°C for 1 h. The alcohol **2** was separated similarly to method A to give a yield of 3.19 g (62%) as colorless crystals with mp 123°C (ethyl acetate) and R_f 0.63. Mass spectrum, *m/z* (*I*, %): M^+ 391 (37), $[M\text{-}C_5H_5N]^{+\cdot} = \Phi_1$ 312 (48), $[\Phi_1\text{-}OH]^{+\cdot}$ 295 (42), $[M\text{-}104]^{+\cdot}$ 287 (51). IR spectrum, ν, cm^{-1}: 3335 (OH). UV spectrum, λ_{max}, nm (log ε): 207 (4.77); 216 (4.7), 228 sh (4.57), 230 sh (4.29); 300 (3.4); 310 (3.36). ^{1}H NMR spectrum, δ, ppm (1:1 mixture of diastereomers): 8.7 and 8.5 (0.5H each, both br. d, J = 4.9 Hz, H-α Py); 7.60-7.05 (8H, m, 5H Ph and 3H Py); 6.85-6.20 (6H, m, H_{arom}, paracycl); 6.2 (1H, s, H-5 arom. paracycl); 5.98 and 5.5 (0.5H each, both s, OH); 3.4-2.5 (8H, m, $H_{aliph.}$). Fluorescence spectrum, λ_{max}, nm: 358. Found, %: C 85.7; H 6.42; N 3.61. $C_{28}H_{25}NO$. Calculated, %: C 85.9; H 6.39; N 3.58. M 391.

α-Pyridyl([2.2]paracyclophan-4-yl)phenylmethanol Cu(II) Chloride (3). A solution of $CuCl_2 \cdot 2H_2O$ (0.2 g, 1.17 mmol) in ethanol (10 ml) was added to a solution of the alcohol **2** (2.3 g, 0.53 mmol) and the mixture was refluxed with stirring for 3 h. The product was cooled and left for 1 day. The precipitate formed was filtered off and dried in air to give the complex **3** (1.32 g, 93%) as emerald colored prismatic crystals with mp 169-170°C (decomp.) (see X-ray data for compound **3)**.

Cyclocondensation of Triarylmethanol 2. Compound **2** (0.4 g, 1 mmol) was refluxed in formic acid as described in the study [1] and the product was separated chromatographically on an alumina column using hexane as eluent. The first product was 1-phenyl-6-aza[3.2.2][1,2,5]-1,1α-dehydro-6H-cyclophano[1,2-*a*]-pyridine (**5**) (0.13 g, 35%) as bright-yellow crystals with mp 218-221°C (hexane) and R_f 0.65. Mass spectrum, *m/z* (*I*, %): $M^{+\cdot}$ 373 (100), $[M\text{-}104]^{+\cdot}$ 269 (65), 104 (7), 43 (23). UV spectrum, λ_{max}, nm (log ε): 208 (4.26); 230 sh (4.15), 260 sh (4.12), 278 sh (4.06), 330 sh (3.16), 350 sh (3.02), 420 (2.88). ^{1}H NMR spectrum, δ, ppm

(*J*, Hz): 2.75 -3.33 (8H, m, $4CH_2$); 6.08 (1H, s, H-17); 6.43 (1H, br. t, *J* = 6.7 and 7.1, H-4); 6.70 (4H, br. s, *J* = 7.0, H-9, H-10, H-19 and 20), 6.90 (1H, br. t, *J* = 6.7 and 8.3, H-3); 7.10 (1H, s, H-12); 7.60 (1H, d, *J* = 8.3, H-2), 7.41-7.71 (5H, m, C_6H_5); 8.28 (1H, d, *J* = 7.1, H-5). Fluorescence spectrum, λ_{max}, nm: 408, 528. Found, %: N 3.68. $C_{28}H_{23}N$. Calculated, %: N 3.75. M 373.

The second product was 10-phenyl[2.2]paracyclophano[4,5-*b*]indolizine (**4**) (0.09 g, 25%) as bright-yellow crystals with mp 174-175°C (hexane) and R_f 0.66. Mass spectrum, *m/z* (*I*, %): M^+ 373 (20), $[M-104]^{+\cdot}$ 269 (100), 104 (15). UV spectrum, λ_{max}, nm (log ε): 208 (5.22), 234 (5.12), 296 (4.34), 320 sh (4.1), 340 (3.32), 350 (3.16), 400 sh (2.25), 420 (2.94), 430 sh (2.83), 440 (2.82), 480 sh (2.15). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.80 (2H, m, H-11); 3.11-3.30 (4H, m, H-12 and 19), 3.90 (2H, m, H-20), 5.40 and 5.90 (1H each, d, *J* = 8.1, H-14 and 15), 6.33 and 6.43 (1H each, d, *J* = 8.3, H-7 and 8), 6.60 (1H, m, H-3); 6.65 (2H, br. s, $J_{1/2}$ = 6.7, H-17 and 18); 6.90 (1H, m, H-2), 7.40 (1H, d, *J* = 7.8, H-1), 7.50-7.60 (5H, m, C_6H_5), 8.45 (1H, d, *J* = 7.7, H-4). Fluorescence spectrum, λ_{max}, nm: 396. Found, %: N 3.8. $C_{28}H_{23}N$. Calculated, %: N 3.75. M 373.

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