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SYNTHESIS OF CYCLOOCTA[2,1-*b*:3,4-*b*']DIQUINOLINE AND CYCLOOCTA[2,1-*b*:3,4-*b*']DI[1,8]NAPHTHYRIDINE, AND X-RAY CRYSTAL STRUCTURES OF CYCLOOCTA[2,1-*b*:3,4-*b*']DIQUINOLINE AND ITS 2:1 COMPLEX WITH COPPER (I) PERCHLORATE

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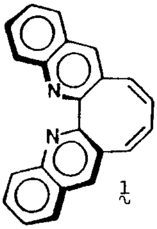
Abstract: New compounds containing a diquinoline or 1,8-dinaphthyridine nucleus fused to the molecular skeleton of cyclooctatetraene have been synthesized. An X-ray analysis of cycloocta[2,1-b:3,4-b']diquinoline (1) has revealed that the molecule contains a C_2 *axis. The reaction of 1 with copper(II) perchlorate furnished a complex of formula* $[(1)_2Cu]ClO_4$*, the coordination geometry about the copper(I) atom being that of a flattened tetrahedron.*

Transition metal complexes containing 2,2'-azabiaryl ligands have aroused a good deal of interest in recent years, mainly because they have found applicability in the domains of photochemistry[3,4,5], biochemistry[6] and organic synthesis[7]. The design and synthesis of novel azabiaryl ligands of C_2 symmetry are thus of importance to a thorough understanding of the potentialities of these complexes. It has been reported that the chain-length of the annelating bridge of a series of 3,3'-annelated 2,2'-diquinolines manipulates the relative orientation of the two quinoline rings and hence influences the geometry of the chelating envelope[8]. In this connection, fusion of a cyclooctatetraene nucleus to 2,2'-azabiaryl ligands will result in novel systems containing an unsaturated annelating bridge with full retention of the required C_2 symmetry axis. Cycloocta[2,1-*b*:3,4-*b*']diquinoline (1) and cycloocta[2,1-*b*:3,4-*b*']di[1,8]-naphthyridine (2) are therefore our target molecules. In conjunction with our long-standing quest for planar eight-membered ring systems[9], it is envisaged that the transition metal complexes of 1 and 2 might possibly comprise such rings. We here report the synthesis of 1 and 2, as well as the X-ray crystallographic studies of 1 and its 2:1 complex 3 with copper(I) perchlorate.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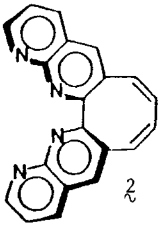
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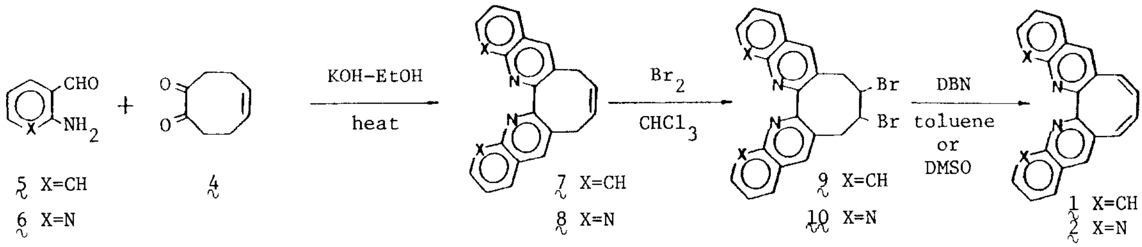
Friedlander's procedure[10] was employed to construct the quinoline and naphthyridine skeleton of 1 and 2. Condensation between the diketone 4[11] and the aminoaldehydes 5[12] and 6[13] provided alkenes 7 and 8 in 63% and 17% yields, respectively[8]. Compound 7 forms colorless crystals (from EtOH), m.p. 257-258°C; ^{1}H-NMR($CDCl_3$) δ 3.10-3.50(m,4H),5.97(t,2H,J=4.0,8.6Hz),



7.57(t,2H,J=8.0,8.3Hz),7.73(t,2H,J=8.0,8.3 Hz), 7.80(d,2H,J=8.3Hz),8.05(s,2H),8.27(d,2H, J=8.3Hz). Compound **8** also forms colorless crystals (from EtOH), m.p.>280°C; ^{1}H-NMR(CDCl$_3$) δ2.40-3.10(m,4H),5.82(dd,2H,J=2.8,8.9Hz),7.52(dd,2H,J=4.2,8.0Hz),8.02(s,2H),8.17(dd,2H,J=2.0, 8.0Hz),9.11(dd,2H,J=2.0,4.2Hz). Bromination of **7** and **8** afforded the corresponding dibromides **9** and **10** in 92% and 88% yields. Dibromide **9** (or **10**) should have two diastereomeric forms which are interconvertable at elevated temperature through a mutarotation process[14]. As the stereochemistry of the dibromide **9** (or **10**) was not important towards the realization of **1** (or **2**), the mixture of the diastereomeric dibromides of **9** (or **10**) was not separated but subjected to direct dehydrobromination with DBN, resulting in the isolation of **1** and **2**, respectively, in 90% and 65% yields. Compound **1** forms colorless crystals (from EtOAc), m.p.261-262°C; ^{1}H-NMR(CD$_3$OD) δ6.62(d.2H,J=10.5Hz),6.89(d,2H,J=10.5Hz),7.61(t,2H,J=6.4,7.9Hz),7.76(t,2H,J=6.4, 8.4Hz),7.90(d,2H,J=7.9Hz), 8.06(s,2H),8.24(d,2H,J=8.4Hz). Compound **2** forms colorless crystals (from EtOH), m.p.>280°C; ^{1}H-NMR(CDCl$_3$) δ6.21(dd,2H,J=2.0,8.0Hz),6.91(dd,2H,J=2.0,8.0Hz),7.52 (dd,2H,J=4.0,8.0Hz),8.01(s, 2H),8.21(dd,2H,J=2.0,8.0Hz),9.12(dd,2H,J=2.0,4.0Hz). Due to their C_2 symmetry (*vide infra*), the ring inversion process of **1** or **2** will not influence the magnetic sites of the nuclei and is therefore not detectable by NMR spectrometry[15]. This is aptly demonstrated by the fact that no signal broadening could be observed for **1** between 25°C and 135°C. Nevertheless, we estimate that the ring inversion barriers of **1** and **2** should be sufficiently high so that their resolutions might be possible[16].

Figure 1 shows a stereo view of the molecular structure of **1**, which has been determined by X-ray crystallography[17]. A crystallographic diad passes through the mid-points of the C(1)-C(1') and C(4)-C(4') bonds. With reference to the geometrical parameters for cyclooctatetraene (C-C single bond 1.475 Å, C=C double bond 1.340 Å, C-C=C angle 126.1°, and C=C-C=C torsion angle 57.9°)[18], the eight-membered ring in **1** exhibits, besides bond-length adjustments caused by annelation to the azabiaryl system, a significantly more folded configuration, as shown by the torsion angles given in the legend. It is noteworthy that the C(3)-C(4)-C(4')-C(3') torsion angle is unusually large and exceeds the N(1)-C(4)-C(4')-N(1') angle by 7°, indicating the presence of steric repulsion between the aromatic rings.

In order to test the practicability of **1** as a chelating ligand and to observe the conformational change of **1** due to transition metal complexation, we have undertaken the preparation of its copper complex. Treatment of **1** with copper(II) perchlorate in EtOH at refluxing temperature and subsequent cooling resulted in the isolation of complex **3** (17% yield based on **1**) of stoichiometry $[(\mathbf{1})_2Cu]ClO_4$. Complex **3** forms dark-reddish crystals from EtOH-H$_2$O, m.p.>300°C; ^{1}H-NMR (CD$_3$COCD$_3$) δ6.54(d,2H,J=10.0Hz),6.85(d,2H,J=10.0Hz),7.37(dd,2H,J=8.0,8.0Hz), 7.47(d,2H,J=8.0Hz) 7.55(dd,2H,J=8.0 ,8.0Hz),7.97(d,2H,J=8.0Hz),8.30(s,2H). 2,2'-Azabiaryl complexes of copper(II) are well-documented[19]. The reason for the reduction of copper(II) to copper(I) is not clear, though it is noted that the $E_{\frac{1}{2}}$ value of the Cu(II)/Cu(I) couple is only 0.61 volt versus $AgNO_3$(0.1M)/Ag[20].

The structure of 3 was unequivocally established by X-ray crystallography[21]. Figure 2 shows a stereo view of the $[(C_{22}H_{14}N_2)_2Cu]^+$ ion in 3 along with important molecular dimensions. The coordination geometry about the metal atom is that of a flattened tetrahedron, with significant deviations from idealized D_2 symmetry. In each organic ligand, the cyclooctatetraene moiety takes the usual tub conformation, which facilitates the alleviation of intramolecular overcrowding in the cation via optimum orientation of the quinoline rings. The much smaller N-C-C-N torsion angles (see lengend), as compared to the observed value in 1, clearly point to a considerable flattening of the ligand molecule through metal coordination.

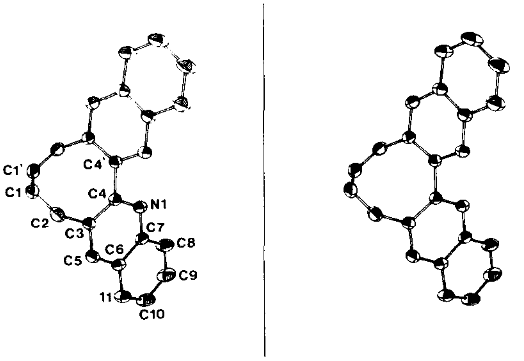


Figure 1. Stereo view of the molecular structure of 1. Selected bond lengths (Å), bond angles (deg), and torsion angles (deg) with e.s.d.'s in parentheses: C(1)-C(1') 1.477(7), C(1)-C(2) 1.321(4), C(2)-C(3) 1.478(4), C(3)-C(4) 1.421(2), C(4)-C(4') 1.507(4), N(1)-C(4) 1.317(3), N(1)-C(7) 1.370(3); C(1')-C(1)-C(2) 125.4(3), C(1)-C(2)-C(3) 125.1(3), C(2)-C(3)-C(4) 123.4(2), C(3)-C(4)-C(4') 120.7(2), C(3)-C(4)-N(1) 124.0(2), N(1)-C(4)-C(4') 115.1(1); C(2')-C(1')-C(1)-C(2) -60.3(5), C(1')-C(1)-C(2)-C(3) -3.2(5), C(1)-C(2)-C(3)-C(4) 61.7(4), C(2)-C(3)-C(4)-C(4') 6.8(4), C(3)-C(4)-C(4')-C(3') -70.0(4), N(1)-C(4)-C(4')-N(1') -62.8(3).

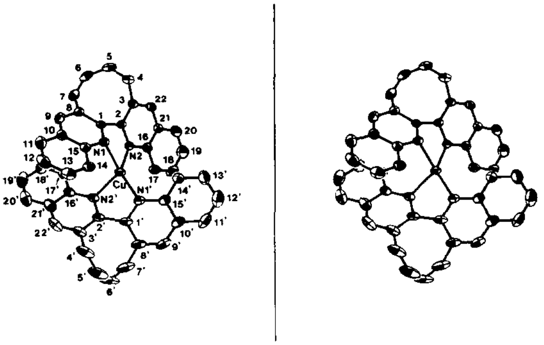


Figure 2. Stereo view of the $[(C_{22}H_{14}N_2)_2Cu]^+$ cation in 3. Selected bond lengths (Å), bond angles (deg), and torsion angles (deg) with e.s.d.'s in parentheses: Cu-N(1) 2.095(4), Cu-N(2) 2.006(4), Cu-N(1') 2.028(4), Cu-N(2') 2.081(4), C(1)-C(2) 1.493(7), C(2)-C(3) 1.426(7), C(3)-C(4) 1.487(7), C(4)-C(5) 1.293(8), C(5)-C(6) 1.442(9), C(6)-C(7) 1.319(8), C(7)-C(8) 1.470(8), C(8)-C(1) 1.423(7), C(1')-C(2') 1.497(8), C(2')-C(3') 1.425(9), C(3')-C(4') 1.501(9), C(4')-C(5') 1.320(11), C(5')-C(6') 1.436(13), C(6')-C(7') 1.350(13), C(7')-C(8') 1.501(9), C(8')-C(1') 1.430(8); N(1)-Cu-N(2) 79.9(2), N(1')-Cu-N(2') 79.8(2), N(1)-Cu-N(1') 127.4(2), N(1)-Cu-N(2') 105.9(2), N(2)-Cu-N(2') 134.6(2), N(2)-Cu-N(1') 132.8(2), C(1)-C(2)-C(3) 125.3(4), C(2)-C(3)-C(4) 124.8(5), C(3)-C(4)-C(5) 128.8(5), C(4)-C(5)-C(6) 127.3(5), C(5)-C(6)-C(7) 127.7(6), C(6)-C(7)-C(8) 129.3(5), C(7)-C(8)-C(1) 126.2(5), C(8)-C(1)-C(2) 125.2(4), C(1')-C(2')-C(3') 126.0(5), C(2')-C(3')-C(4') 123.4(6), C(3')-C(4')-C(5') 126.2(7), C(4')-C(5')-C(6') 128.1(7), C(5')-C(6')-C(7') 126.5(7), C(6')-C(7')-C(8') 126.6(7), C(7')-C(8')-C(1') 124.1(6), C(8')-C(1')-C(2') 125.4(5); N(1)-C(1)-C(2)-N(2) 39.0(6), N(1')-C(1')-C(2')-N(2') 36.9(7), C(8)-C(1)-C(2)-C(3) 53.4(7), C(2)-C(3)-C(4)-C(5) -62.3(9), C(4)-C(5)-C(6)-C(7) 51.0(11), C(6)-C(7)-C(8)-C(1) -56.0(9), C(8')-C(1')-C(2')-C(3') 52.9(9), C(2')-C(3')-C(4')-C(5') -64.7(10), C(4')-C(5')-C(6')-C(7') 53.9(14), C(6')-C(7')-C(8')-C(1') -62.4(10).

References and Notes

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17. Compound **1**, formula $C_{22}H_{14}N_2$, FW = 306.36. Monoclinic, space group $C2/c$, a = 17.383(5), b = 7.509(2), c = 16.016(3) Å, β = 130.75(1)°, V = 1583.7(5) Å^3, Z = 4, D_m = 1.288 g cm^{-3} (flotation in aqueous KI), D_c = 1.285 g cm^{-3}, μ(Mo $K\alpha$) = 0.71 cm^{-1}. Nicolet R3m diffractometer, monochromatized Mo $K\alpha$ radiation (λ = 0.71069 Å), ω-2θ variable scan mode, $2\theta_{max}$ = 54°, 1444 unique data. All 12 nonhydrogen atoms in the asymmetric unit were subjected to anisotropic refinement, and H atoms were included in structure factor calculations. Refinement of 1135 observed data [$|F_o|>3\sigma(|F_o|)$] on 109 variables yielded R = 0.052. The atomic parameters have been deposited with the Cambridge Crystallographic Data Centre.
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21. Complex **3**, formula $C_{44}H_{28}N_4CuClO_4$, FW = 775.71, space group $P2_1/n$ a = 8.517(2), b = 16.854(2), c = 24.867(5) Å, β = 92.90(2)°, V = 3565(1) Å^3, Z = 4, D_m = 1.455 g cm^{-3} (flotation in aqueous KI), D_c = 1.455 g cm^{-3}. Nicolet R3m diffractometer, Mo $K\alpha$ radiation (λ = 0.71069 Å), $2\theta_{max}$ = 50°, 5365 reflections measured, transmission factors 0.712-0.742 applied in absorption correction. Refinement of 3773 observed reflection on [$|F_o|>3\sigma(|F_o|)$] 487 variables yielded R = 0.070 and R_w = 0.092. The atomic parameters have been deposited with the Cambridge Crystallographic Data Centre.

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