

A New System of Ionophors Derived from *o,o'*-Biphenyldiol
X-Ray Structure of *o*-Hydroxy-biphenyl-*o'*-oxyacetamide

Whei Oh Lin, J. B. N. da Costa

Seção de Química, Instituto Militar de Engenharia,
 Praia Vermelha, Urca, Rio de Janeiro, RJ,
 Brasil, 22290

Helmut G. Alt*

Laboratorium für Anorganische Chemie,
 Universität Bayreuth, Universitätsstraße 30,
 D-8580 Bayreuth, Federal Republic of Germany

Robin D. Rogers

Department of Chemistry,
 Northern Illinois University,
 DeKalb, Illinois, 60115 (U.S.A.)

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Noncyclic Ionophors, X-Ray,
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The synthesis of mono- and diacetamides starting with *o,o'*-biphenyldiol is described. From *o*-hydroxy-biphenyl-*o'*-oxyacetamide an X-ray structure could be obtained.

yields mono- and dialkylated products of type **1** and **2** [4].

The diethyl derivatives **1a** and **2a** can complex Zn^{2+} , Mn^{2+} , Fe^{3+} and Co^{2+} cations but not K^+ . Only **2a** can complex Ca^{2+} .

The X-ray structure of **1a** [5] (Fig. 1) shows that the phenyl rings form an angle of 53.18° . The hydrogen of the hydroxy function occupies a bridging posi-

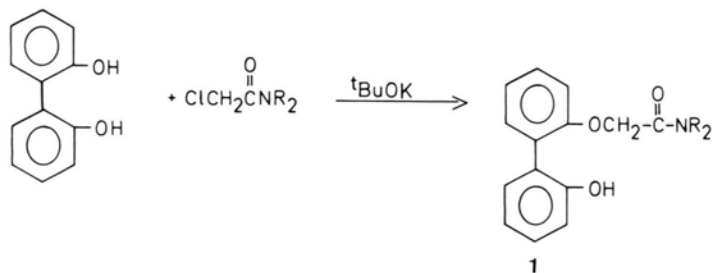
Table I. Final fractional coordinates for $C_{18}H_{21}NO_3$.

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>a</i> _{B(eqv)}
O(1)	0.0514(7)	0.5000	0.5838(2)	4.01
O(2)	0.4018(6)	0.3880(7)	0.6370(2)	3.72
O(3)	0.3083(7)	0.3073(8)	0.5419(2)	3.65
N	0.6172(8)	0.2271(8)	0.5213(2)	3.43
C(1)	0.007(1)	0.548(1)	0.6327(3)	4.00
C(2)	-0.076(1)	0.680(1)	0.6334(4)	4.70
C(3)	-0.140(1)	0.738(1)	0.6786(4)	6.28
C(4)	-0.112(1)	0.666(1)	0.7249(4)	6.03
C(5)	-0.031(1)	0.533(1)	0.7248(3)	5.34
C(6)	0.029(1)	0.471(1)	0.6783(3)	3.83
C(7)	0.104(1)	0.326(1)	0.6792(3)	3.76
C(8)	-0.014(1)	0.225(1)	0.7038(3)	4.81
C(9)	0.045(2)	0.089(1)	0.7042(3)	5.39
C(10)	0.217(2)	0.046(1)	0.6811(3)	5.36
C(11)	0.340(1)	0.145(1)	0.6578(3)	4.31
C(12)	0.284(1)	0.282(1)	0.6568(3)	3.51
C(13)	0.5662(9)	0.3498(9)	0.6049(2)	3.56
C(14)	0.487(1)	0.291(1)	0.5531(3)	3.30
C(15)	0.546(1)	0.176(1)	0.4712(2)	4.19
C(16)	0.575(1)	0.284(1)	0.4286(3)	6.58
C(17)	0.8323(9)	0.209(1)	0.5331(3)	4.42
C(18)	0.884(1)	0.071(1)	0.5545(3)	5.06

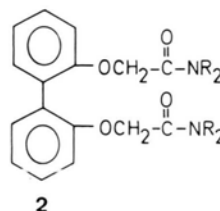
$$a_{B(eqv)} = 4/3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$$

Recently we have shown that phenylenedioxy-diacetamides and their saturated analogues can function as ionophors for certain metal cations [1–3]. We now report the synthesis of a new system of potential ligands derived from *o,o'*-biphenyldiol.

The reaction of *o,o'*-biphenyldiol with an appropriate chloroacetamide and potassium *tert*-butoxide



R = alkyl, aryl,
Et(a)



* Reprint requests to Prof. Dr. H. G. Alt.

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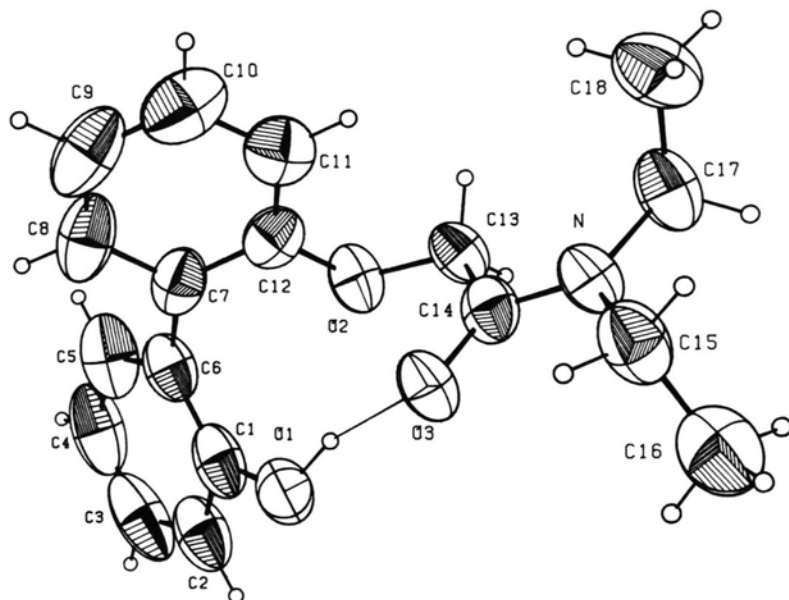


Fig. 1. ORTEP plot of the molecular structure of **1a** showing 50% probability ellipsoids. Selected bond distances (Å) and angles (°): O(1)–C(1) 1.368(9), O(2)–C(12) 1.384(8), O(2)–C(13) 1.418(7), O(3)–C(14) 1.236(7), N–C(14) 1.341(7), O(1)–H(1) 0.98(7), O(3)–H(1) 1.80(7), O(1)–H(1)–O(3) 159(6).

tion *via* a hydrogen bond to the carbonyl oxygen of the acetamide group.

It is very likely that the mutual orientation of the two phenyl rings adjusts to the entering cation upon complexation.

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- [1] W. O. Lin, M. C. B. V. de Souza, and H. G. Alt, *Z. Naturforsch.* **39b**, 1375 (1984).
- [2] W. O. Lin and H. G. Alt, *Z. Naturforsch.* **40b**, 441 (1985).
- [3] W. O. Lin, M. C. B. V. de Souza, and H. G. Alt, *Z. Naturforsch.* **43b**, 165 (1988).
- [4] Spectroscopic data: ^1H NMR (δ [ppm] in CDCl_3). **1a**: 8.38 (s, OH); 6.60–7.40 (m, 8H); 4.81 (s, $-\text{OCH}_2-$); 3.26/3.40 (q, $-\text{NCH}_2-$); 1.23/1.12 (t, $-\text{CH}_3$). **2a**: 7.26–7.40 (m, 4H); 6.95–7.10 (m, 4H); 4.60 (s, $-\text{OCH}_2-$); 3.20/3.33 (q, $-\text{NCH}_2-$); 0.97/1.09 (t, [$J(\text{HH}) = 7.2$ Hz], $-\text{CH}_3$). ^{13}C NMR (δ [ppm] in CDCl_3). **1a**: 167.1 (C=O); 154.7, 154.0, 132.7, 131.0, 129.1, 128.8, 127.9, 126.0, 121.9, 120.1, 117.8, 109.7 (biphenyl); 63.4 ($-\text{OCH}_2-$); 40.7/40.5 ($-\text{NCH}_2-$); 14.2/12.8 ($-\text{CH}_3$). **2a**: 167.3 (C=O); 155.8, 131.7, 128.7, 128.1, 121.3, 113.0 (biphenyl); 69.0 ($-\text{OCH}_2-$); 41.4, 40.0 ($-\text{NCH}_2-$); 14.0, 12.7 ($-\text{CH}_3$).
- [5] Crystallographic data for **1a**: space group, $\text{Pn}2_1\text{a}$ (an

alternate setting of $\text{Pna}2_1$, No. 33), $a = 6.6720(6)$, $b = 9.620(2)$, $c = 25.583(7)$ Å, $Z = 4$, D (calcd) = 1.21 g cm^{-3} , μ (calcd) = 0.47 cm^{-1} . A total of 738 unique, observed [$F_o \geq 5\sigma(F_o)$] reflections were collected at 20 °C with an Enraf-Nonius CAD-4 diffractometer (Mo– $\text{K}\alpha$, λ 0.71073 Å, max. 2θ 50°). The structure was solved by direct methods (MULTAN 80) and completed by syntheses. The geometrically constrained hydrogen atoms were placed in calculated positions at a distance of 0.95 Å from the bonded carbon atom. The OH-hydrogen was located in a difference map and refined isotropically, while all other atoms were refined anisotropically. $R = 0.039$, $R_w = 0.039$. Fig. 1 shows the molecular structure and gives some important distances and angles, Table I contains the atomic coordinates and equivalent isotropic displacement parameters. Further crystal structure data may be obtained from the Fachinformationszentrum Energie, Physik, Mathematik, D-7514 Eggenstein-Leopoldshafen, code CSD 53740.