

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

Helmuth 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.)

Z. Naturforsch. **44b**, 1331–1332 (1989);
 received February 2/April 28, 1989

Noncyclic Ionophors, X-Ray,
o-Hydroxy-biphenyl-*o'*-oxyacetamide

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.

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

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

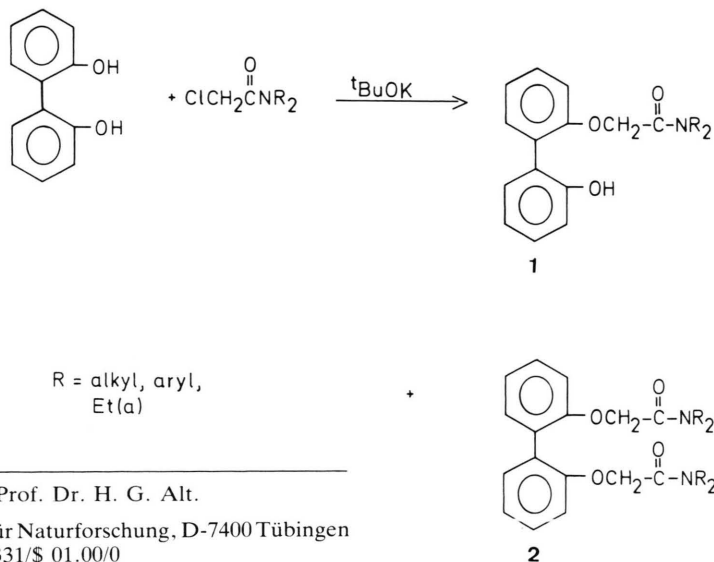
The diethyl derivatives **1a** and **2a** can complex Zn^{2+} , Mn^{2+} , Fe^{3+} and Co^{2+} cations but not K^+ . Only **2a** can complex Ca^{2+} .

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 $\text{C}_{18}\text{H}_{21}\text{NO}_3$.

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

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



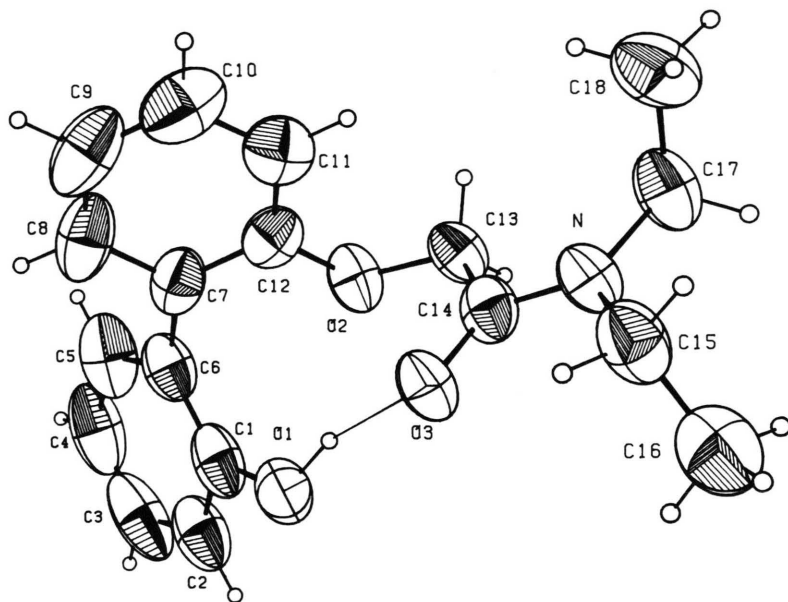


Fig. 1. ORTEP plot of the molecular structure of **1a** showing 50% probability ellipsoids. Selected bond distances (Å) and angles (°): O(1)–C(1) 1.368(9), O(2)–C(12) 1.384(8), O(2)–C(13) 1.418(7), O(3)–C(14) 1.236(7), N–C(14) 1.341(7), O(1)–H(1) 0.98(7), O(3)–H(1) 1.80(7), O(1)–H(1)–O(3) 159(6).

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.

We thank the Volkswagen Foundation and the Conselho Nacional de Pesquisa e Desenvolvimento (CNPq) for financial support and the U.S. National Science Foundation Chemical Instrumentation Program for the diffractometer (R.D.R.).

- [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–K α , 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.