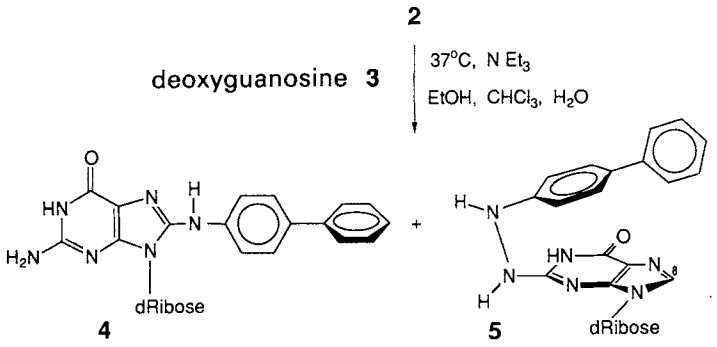

7.0) and ethanol at 50°C.[8] The assumption that **2** is the reactive species in this reaction is confirmed by our findings.[9]

Experimental

2: A suspension of 4.00 g (21.6 mmol) of **1** in diethyl ether (50 mL) and triethylamine (2.9 mL, 21.6 mmol) cooled to −40°C was treated with a solution of acetyl cyanide [10] (1.50 g, 21.6 mmol) in diethyl ether (30 mL) and the mixture vigorously stirred for 2 h between −40° and −10°C. After extraction with ice-water the aqueous phase was extracted at 0°C with 50 mL of CH_2Cl_2, the organic phases combined, dried with $MgSO_4$, and the solvent removed in a rotary evaporator at 0°C. The residue was rapidly dissolved at room temperature in 100 mL of ether/petroleum ether (1/1) and 20 mL of CH_2Cl_2 and recrystallized at −30°C. The bright yellow crystals of **2** were dried at −20°C. Yield 3.98 g (81%); correct elemental analysis (C,H,N). ^{1}H NMR (400 MHz, $CDCl_3$, 230 K): δ = 2.27 (s, 3H), 7.15 (d, 2H), 7.38 (t, 1H), 7.47 (t, 2H), 7.58 (2d, 4H), 8.90 (N−H, 1H). ^{13}C NMR (400 MHz, $CDCl_3$, 230 K): δ = 19.3, 116.9, 126.7, 127.0, 127.7, 128.7, 136.7, 140.1, 145.4, 170.8. IR (Nujol): $\tilde{\nu}$ = 3245, 1755, 1223 cm^{-1}.

Reaction of **2** with **3**: **2** (909 mg, 4.00 mmol) was treated with a solution of **3** (1.07 g, 4.00 mmol) and triethylamine (455 mg, 4.50 mmol) in 70 mL of ethanol/$CHCl_3$/water (7/3/4) at 37°C. After 1 h the solvent was removed; the adducts **4** and **5** were first separated over a silica gel column with $CHCl_3$/ethanol (7/3) and then by preparative HPLC [11]. Yield (after silica gel chromatography): **4**: 112 mg (6%); ^{1}H NMR ([D$_6$]DMSO, 400 MHz: the data agree with those quoted in Ref. [7a]. ^{13}C NMR: δ = 38.4, 61.2, 71.2, 82.8, 87.2, 112.1, 117.6, 125.9, 126.5, 126.6, 128.7, 132.2, 140.0, 140.3, 143.1, 149.5, 153.0, 155.9. MS (FD): *m/z* 434 (100%, $M^{\oplus}$), 318 (61%, $M^{\oplus}$ − dRibose + H). IR (KBr): $\tilde{\nu}$ = 3329, 2927, 1680, 1562, 1356, 1024, 960, 764, 698 cm^{-1}; **5**: 55 mg (3%); ^{1}H NMR ([D$_6$]DMSO, 400 MHz): δ = 2.12 (m, 1H), 2.42 (m, 1H), 3.47 (m, 2H), 3.76 (m, 1H), 4.28 (m, 1H), 4.91 (s, OH), 5.21 (s, OH), 5.95 (dd, 1H), 6.35 (s, 2H, −NH−NH−), 7.37 (d, 2H), 7.37 (t, 1H), 7.40 (s, 1H), 7.48 (t, 2H), 7.65, 7.66 (2d, 4H), 8.24 (s, 1H, NH); the singlet of H-8 of the deoxyguanosine part of **5** (δ = 7.40) is shifted markedly upfield compared to that of **3** ([D$_6$]DMSO, 300 MHz, δ = 7.94) and other purine nucleosides and nucleotides (see C. J. Pouchert, J. R. Campbell: *The Aldrich Library of NMR Spectra, Vol. 8*, Aldrich Chemical Company, Milwaukee 1974). This suggests a folded conformation for **5** in which the biphenyl moiety lies above the guanine part of the molecule and thus provides for the shielding of H-8. A similar folded conformation was found for methotextrate in an unpolar solvent (P. Faupel, V. Buss, *Angew. Chem. 100* (1988) 422; *Angew. Chem. Int. Ed. Engl. 27* (1988) 423). ^{13}C NMR: δ = 61.8 (t, ^1J(C-H) = 140.0 Hz), 70.7 (d, ^1J(C-H) = 149.9 Hz), 82.0 (d, ^1J(C-H) = 163.5 Hz), 87.2 (d, ^1J(C-H) = 147.2 Hz), 125.0 (s), 126.5 (d, ^1J(C-H) = 159.5 Hz), 126.6 (d, ^1J(C-H) = 159.7 Hz), 127.0 (s), 127.4 (d, ^1J(C-H) = 212.6 Hz), 127.4 (d, ^1J(C-H) = 162.6 Hz), 128.3 (d, ^1J(C-H) = 162.4 Hz), 128.9 (d, ^1J(C-H) = 161.7 Hz), 138.3 (s), 139.0 (s), 139.6 (s), 148.8 (s), 155.4 (s); the C-2 signal of the dRibose moiety is covered by DMSO signals. MS (FD): *m/z* 434 (100%, $M^{\oplus}$), 318 (78%, $M^{\oplus}$ − dRibose + H); IR (KBr): $\tilde{\nu}$ = 3334, 2924, 1658, 1522, 1487, 1333, 1086, 1049, 764, 698 cm^{-1}. UV: λ_{max} = 251, 216 nm.

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CAS Registry numbers:
1, 6810-26-0; **2**, 119273-47-1; **3**, 961-07-9; **4**, 84283-08-9; **5**, 117205-56-8; CH_3COCN, 631-57-2; *N*-(4-biphenylyl)-*O*-pivaloylhydroxylamine, 119273-48-2.

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[2] J. W. Gorrod, L. A. Damani: *Biological Oxidation of Nitrogen in Organic Molecules*, VCH Verlagsgesellschaft, Weinheim 1985.

[3] a) H. Bartsch, M. Dworkin, J. A. Miller, E. C. Miller, *Biochim. Biophys. Acta 286* (1972) 272; see also b) E. Kriek, *ibid. 335* (1974) 177; c) C. M. King, *Cancer Res. 34* (1974) 1403; d) E. C. Miller, *ibid. 38* (1978) 1479; e) F. A. Beland, W. T. Allaban, F. E. Evans, *ibid. 40* (1980) 834; f) E. C. Miller, J. A. Miller, *Cancer (Amsterdam) 47* (1981) 2327; g) I. B. Glowinski, L. Savage, M.-S. Lee, C. M. King, *Carcinogenesis 4* (1983) 67; h) S. S. Thorgeirsson in H. Greim, R. Jung, M. Kramer, H. Marquardt, F. Oesch (Eds.): *Biochemical Basis of Chemical Carcinogenesis*, Raven Press, New York 1984, p. 47; i) T. J. Flammang, F. F. Kadlubar, *Carcinogenesis 7* (1986) 919; j) C.-C. Lai, E. C. Miller, J. A. Miller, A. Liem, *ibid. 9* (1988) 1295.

[4] L. Rehn, *Arch. Klin. Chir. 50* (1895) 588.

[5] *N*-Acetoxy compounds of other mutagenic and carcinogenic aromatic amines which were prepared in solution but not isolated and characterized: a) Y. Hashimoto, K. Shudo, T. Okamoto, *J. Am. Chem. Soc. 104* (1982) 7636; *Biochem. Biophys. Res. Commun. 96* (1980) 355; *92* (1980) 971; b) K. B. Delclos, W. G. Tarpley, E. C. Miller, J. A. Miller, *Cancer Res. 44* (1984) 2540; c) A. M. Lobo, M. M. Marques, S. Prabhakar, H. S. Rzepa, *J. Chem. Soc. Chem. Commun. 1985*, 1113; *J. Org. Chem. 52* (1987) 2925. Prepared in solution, characterized, but not isolated: 4-(acetoxyamino)quinoline 1-oxide: d) Y. Kawazoe, O. Ogawa, G.-F. Huang, *Tetrahedron 36* (1980) 2933; e) M. Demeunynck, N. Thome, M.-F. Lhomme, J. M. Mellon, J. Lhomme, *J. Am. Chem. Soc. 108* (1986) 3539, and references cited therein. Obtained in substance and characterized *O*-acetyl-*N*-arylhydroxylamines: f) W. Borsche, *Ber. Dtsch. Chem. Ges. 56* (1923) 1494; g) A. C. Huggett, J. L. Cone, S. S. Thorgeirsson, P. P. Roller, *J. Org. Chem. 52* (1987) 4933; h) G. Boche, F. Bosold, S. Schröder, *Angew. Chem. 100* (1988) 965; *Angew. Chem. Int. Ed. Engl. 27* (1988) 973; i) *O*-acetyl-*N*-(2-naphthyl)hydroxylamine: M. Famulok, F. Bosold, G. Boche, *Tetrahedron Lett.*, in press. We have also allowed **2** to react with *N*-methylaniline in analogy to the results described in Refs. [5h, i]: M. Famulok, F. Bosold, G. Boche, unpublished.

[6] Analogously to **2**, we have prepared and characterized *N*-(4-biphenylyl)-*O*-pivaloylhydroxylamine and allowed it to react with **3**; **4** and **5** were obtained in similar yields as in the case of **2**; M. Famulok, F. Bosold, G. Boche, unpublished.

[7] a) F. F. Kadlubar, F. A. Beland, D. T. Beranek, K. L. Dooley, R. H. Heflich, F. E. Evans in T. Sugimura, S. Kondo, H. Takebe (Eds.): *Environmental Mutagens and Carcinogens*, A. R. Liss, New York 1982, p. 385; b) F. A. Beland, D. T. Beranek, K. L. Dooley, R. H. Heflich, F. F. Kadlubar, *EHP Environ. Health Perspect. 49* (1983) 125; the authors assume hydroxylamine **1** as reactive metabolite which is formed from the *N*-glucuronide of **1** in the acid medium of the urine and reacts further after protonation at the oxygen; c) a review of "DNA adducts of aromatic amines" is given in H.-G. Neumann, *J. Cancer Res. Clin. Oncol. 111* (1986) 100.

[8] a) R. Shapiro, G. R. Underwood, H. Zawadzka, S. Broyde, B. E. Hingerty, *Biochemistry 25* (1986) 2198. These authors also allowed *O*-acetyl-*N*-(4-biphenylyl)-*N*-trifluoroacetylhydroxylamine to react with the dinucleotide d(CpG) under the same conditions at 37°C and obtained the adduct d(CpG$^{8\text{-ABP}}$); b) with the tetranucleotide 5′-d(TpGpCpA)-3′, the adduct 5′-d(TpG$^{8\text{-ABP}}$pCpA)-3′ was found: D. D. Lasko, A. K. Basu, F. F. Kadlubar, F. E. Evans, J. O. Lay, Jr., J. M. Essigmann, *ibid. 26* (1987) 3072.

[9] **4** and **5** were also obtained when the hydroxylamine **1** was allowed to react with DNA at pH 5 and the DNA finally cleaved enzymatically [7]; upon feeding rats with *N*-acetyl-*N*-(4-biphenylyl)hydroxylamine, **4** was detected with the help of a ^{32}P-post-labeling assay: R. C. Gupta, N. R. Dighe, *Carcinogenesis 5* (1984) 343.

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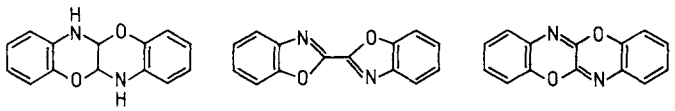
[11] LiChrosorb RP 18, 7 μm, preparative HPLC column (20 × 230 mm), isocratic elution with methanol/water (1/1).

Photochemical Formation of a Stable Oxalic Acid Orthoamide with a Propellane Structure

By *Erich Tauer,* Karl-Heinz Grellmann, Mathias Noltemeyer,* and *George M. Sheldrick*

We have recently reported[1] that the condensation of glyoxal with 2-aminophenol does not give 2,2′,3,3′-tetrahy-

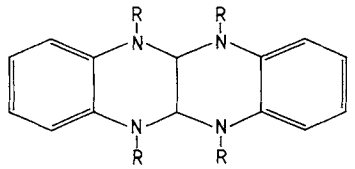
[*] Dr. E. Tauer, Dr. K. H. Grellmann
Max-Planck-Institut für Biophysikalische Chemie,
Abt. Spektroskopie
Am Fassberg, D-3400 Göttingen (FRG)
Dr. M. Noltemeyer, Prof. G. M. Sheldrick
Institut für Anorganische Chemie der Universität
Tammannstrasse 4, D-3400 Göttingen (FRG)



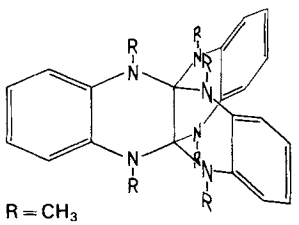
1 2 3

dro-2,2'-bibenzoxazole as was previously assumed, but affords, instead, 5a,6,11a,12-tetrahydro[1,4]benzoxazino[3,2-*b*][1,4]benzoxazine **1**. Exposure of an air-saturated solution of **1** in an inert solvent (e.g., cyclohexane) to long wavelength light ($\lambda \geq 260$ nm) leads to the formation of 2,2'-bibenzoxazole **2**; when the photolysis is performed with short wavelength light ($\lambda < 260$ nm), [1,4]benzoxazino[3,2-*b*][1,4]benzoxazine **3** is formed additionally.

In order to study the mechanism of this photooxidation reaction in more detail, we prepared derivatives and analogues of **1**, for example, the compound 5,5a,6,11,11a,12-hexahydro-5,6,11,12-tetramethyl-quinoxalino[2,3-*b*]quinoxaline **4** which has not yet been described in the literature.



4



5

R = CH_3

Compound **4** exhibits very surprising photochemical properties. Irradiation of a nitrogen-purged solution of **4** in cyclohexane with light of wavelength $\lambda = 254$ nm yields the oxalic acid orthoamide **5** in 11% chemical yield along with other, as yet uncharacterized photoproducts. **5** is a stable compound and can be recrystallized from ethanol. It absorbs similarly to **4** in the UV and has an unstructured fluorescence spectrum. An X-ray structure analysis[2] (Fig. 1) showed that **5** has a [4,4,4]-propellane structure with the molecule lying with C1 and C10 on a crystallographically exact threefold symmetry axis (symmetry position x,x,x); the molecular symmetry is D_3. The difference electron density map showed additional maxima which were assigned to a disordered solvent molecule (ethanol), whose presence was also indicated by the elemental analysis.

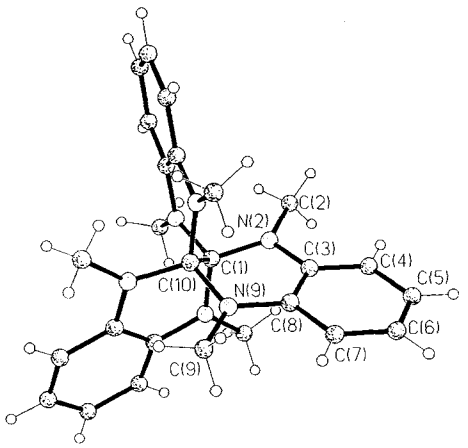


Fig. 1. Molecular structure of **5**. Selected bond lengths [pm] and angles [°]: C1-C10 157.9(7), C1-N2 144.5(3), C10-N9 145.1(3), C2-N2 145.0(5), C3-C4 138.9(5), C4-C5 138.5(7), C5-C6 134.8(8), C6-C7 137.8(6), C3-C8 141.7(5); N2-C1-C10 107.2(2), C1-N2-C2 121.6(3), N2-C3-C8 120.0(3), C1-C10-N9 107.4(2).

Nothing is known about the mechanism of the photoreaction **4** → **5**. To the best of our knowledge, **5** is the first orthoamide derivative of oxalic acid with the substitution pattern of a hexaminoethane.

Experimental Procedure

4: *N,N'*-dimethyl-N,N'-ditosyl-*o*-phenylenediamine [3] (88 g, 0.2 mol) was heated in a mixture of H_2SO_4 (80 mL) and H_2O (8 mL) for 5 h, after which the solution was poured into 300 mL of ice water [4]. The resulting solution was allowed to flow under N_2 into 1 L of NaOH (6 M) and the free amine was steam distilled under N_2 into a light-protected receiving flask. After ca. 3 L of liquid had been collected, 19.2 g of a 30% aqueous solution of glyoxal (0.1 mol) was added to the amine-water emulsion with rapid stirring. After stirring for a further 48 h, the crude product was collected by filtration, washed with H_2O, and dried. Yield: 19 g (65%), m.p. 160–164°C. Recrystallizing three times from 2-propanol (1 g/50 mL) under N_2 afforded colorless crystals of **4** (14.3 g, m.p. 167–169°C). ^{1}H NMR (80 MHz, $CDCl_3$): $\delta = 2.98$ (s, 12H, CH_3), 4.28 (s, 2H, CH), 6.5 (m, 8H, arylH); UV (C_6H_{12}): λ_{max}/nm ($\log\varepsilon$) = 312 (4.11), 257 (4.14), 227 (4.81). Correct elemental analysis.

5: A solution of **4** (1 g) in p.a. cyclohexane (1.3 L) was photolyzed (48 h) in a Rayonet reactor under N_2 using 16 lamps ($\lambda = 254$ nm). After removal of the solvent on a rotary evaporator, the mixture was separated chromatographically (Al_2O_3, cyclohexane/diisopropyl ether 3/1). It yielded 520 mg of unreacted **4** and, after recrystallization from ethanol, 53 mg (11%) of **5** as colorless crystals, m.p. 272–273°C. MS: $m/z = 426$ ($M^{\oplus}$); ^{1}H NMR (80 MHz, $CDCl_3$): $\delta = 2.7$ (s, 18H, CH_3), 6.5–6.85 (m, 12H, arylH); UV (C_6H_{12}): λ_{max}/nm ($\log\varepsilon$) = 316 (4.38), 310 (4.34), 250 (4.33, sh), 227 (4.99); fluorescence: $\lambda_{max} = 347$ nm (line width 50 nm). Correct elemental analysis.

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CAS Registry numbers:
4, 13784-23-1; **5**, 118894-97-6; *N,N'*-dimethyl-*N,N'*-ditosyl-*o*-phenylenediamine, 29627-62-1; glyoxal, 107-22-2.

[1] E. Tauer, K. H. Grellmann, E. Kaufmann, M. Noltemeyer, *Chem. Ber. 119* (1986) 3316.

[2] **5**·0.5 EtOH: cubic, space group $Pa\bar{3}$, $a = 1677.6(5)$ pm, $V = 4.7213$ nm^3, $Z = 8$, $\rho_{calcd} = 1.299$ g cm^{-3}, $\mu = 0.08$ mm^{-1} ($Mo_{K\alpha}$); 6934 intensities measured to $2\theta = 45°$, 968 symmetry independent reflections with $F > 3\sigma(F)$ used in the structure solution (SHELXS-86) and refinement (SHELX-76), non-hydrogen atoms anisotropic and H atoms as rider model, $R = 0.090$, $wR = 0.092$, $w^{-1} = \sigma^2 + 0.0008F^2$. Further details of the crystal structure investigation may be obtained from the Fachinformationszentrum Energie, Physik, Mathematik GmbH, D-7514 Eggenstein-Leopoldshafen 2 (FRG), on quoting the depository number CSD-53369, the names of the authors, and the journal citation.

[3] Synthesis according to H. Stetter, *Chem. Ber. 86* (1953) 161.

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(tBuSiP)$_4$—The First Silaphosphacubane**

By *Marianne Baudler,* Guido Scholz, Karl-Friedrich Tebbe,* and *Magda Fehér*

Although a large number of phosphorus-silicon heterocycles having various molecular frameworks are already known,[1,2] a silaphosphane with a cubane structure has yet to be reported. We have now prepared the first silaphosphacubane, *closo*-tetrakis(*tert*-butylsilylphosphane) **1**, and

[*] Prof. Dr. M. Baudler, G. Scholz, Prof. Dr. K.-F. Tebbe, Dr. M. Fehér
Institut für Anorganische Chemie der Universität
Greinstrasse 6, D-5000 Köln 41 (FRG)

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