

Synthesis and Crystal Structure of 1,1-Dimethoxy-4,4-bis(phenylamino)-3-buten-2-one

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The crystal structure of 1,1-dimethoxy-4,4-bis(phenylamino)-3-buten-2-one (I) has been determined. There are two symmetrically independent molecules in the crystal lattice with some differences in the bond lengths, angles and torsion angles. The nitrogen atoms are nearly planar and π -delocalization exists in I. In the crystal structure, two different parallel infinite chains are produced by N–H...O hydrogen bonds, each of them containing one of the two independent molecules.

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α -Oxoketene-*N,N*-acetals have been used as versatile three-carbon synthons for the synthesis of various organic compounds.¹ Due to the electron-donating ability of the amino groups and the electron-withdrawing ability of the carbonyl group, the C=C bonds in these compounds are highly polarized. This gives rise to an increase in the bond length of the C=C bond and an increase in the electron density at the α -carbon atom.² In spite of their extensive applications in organic synthesis, the structure for this type of compound has been rarely investigated using X-ray crystallography.³ In the present work, the crystal structure of a new compound in this category, 1,1-dimethoxy-4,4-bis(phenylamino)-3-buten-2-one (I), was determined. α -Oxoketene-*N,N*-acetal I was prepared by modifying a literature method.⁴ Aniline (30 mmol) was converted into its *N*-anion by a reaction with *n*-BuLi (15% in hexane; 45 mmol) in dry THF (50 mL), under a nitrogen atmosphere at -78°C . To this solution, α -oxoketene-*S,S*-acetal⁵ (compound A, Fig. 1) (10 mmol) in dry THF (25 mL) was added. Then, the reaction mixture was refluxed for 24 h to complete the reaction. The work-up procedure was conducted as stated in the literature⁵ to yield I as the major product in 75% yield (white solid, mp 129–131°C), Fig. 1. Single crystals of I were obtained from a solution of ethanol after slow evaporation at room temperature. The crystal and experimental data are given in Table 1. The structure was solved by direct methods. The positions of the hydrogen atoms were obtained from a difference Fourier map. The atomic coordinates for non-hydrogen atoms are listed in Table 2. Selected bond lengths and angles are given in Table 3.

The title compound was obtained as two symmetrically independent molecules (Fig. 2) in the crystal lattice with some differences in bond lengths, angles and torsion angles (for example, compare the torsion angles O(6)–C(34)–C(33)–O(4) = $-170.80(17)^\circ$ and O(5)–C(34)–C(33)–O(4) = $-44.9(2)^\circ$ with the corresponding angles O(3)–C(16)–C(15)–O(1) = $179.87(17)^\circ$ and

O(2)–C(16)–C(15)–O(1) = $-54.6(2)^\circ$ in the other molecule). N(1), N(2), N(3) and N(4) atoms are nearly planar, the angles $\angle\text{C}(6)\text{--N}(1)\text{--C}(13)$, $\angle\text{C}(12)\text{--N}(2)\text{--C}(13)$, $\angle\text{C}(30)\text{--N}(4)\text{--C}(31)$ and $\angle\text{C}(31)\text{--N}(3)\text{--C}(24)$ are $123.9(2)^\circ$, $128.6(2)^\circ$, $123.01(19)^\circ$ and $129.7(2)^\circ$. Due to π -delocalization, the C(13)–C(14) and C(31)–C(32) bond lengths are longer than the normal C–C double bond lengths ($1.415(3)\text{Å}$ and $1.412(3)\text{Å}$, respectively) and the C(14)–C(15) and C(32)–C(33) are shorter than the normal C–C single bond lengths ($1.386(3)\text{Å}$ and $1.380(3)\text{Å}$, respectively).

Table 1 Crystal data and structure refinement for the title compound

Formula: C ₁₈ H ₂₀ N ₂ O ₃	
Formula weight = 312.36	
Crystal system: monoclinic	
Space group: C2/c	Z = 16
a = 22.579(7)Å	β = 93.780(6)°
b = 21.976(7)Å	
c = 13.478(4)Å	
V = 6673(3)Å ³	
D _x = 1.244 Mg/m ³	
No. of reflections used = 6884	
2 θ _{max} = 53.02 with Mo K α	
R = 0.0430 [3370 refs. I > 2 σ (I)]	
(Δ / σ) _{max} = 0.000	
($\Delta\rho$) _{max} = 0.225 eÅ ⁻³	
($\Delta\rho$) _{min} = -0.195 eÅ ⁻³	
Measurement: Bruker SMART	
Program system: SADABS	
Structure determination: SHELXS-97, SHELXL-97, SHELXTL	
Refinement: Full-matrix least-squares on F ²	

CCDC 299816 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data-request/cif

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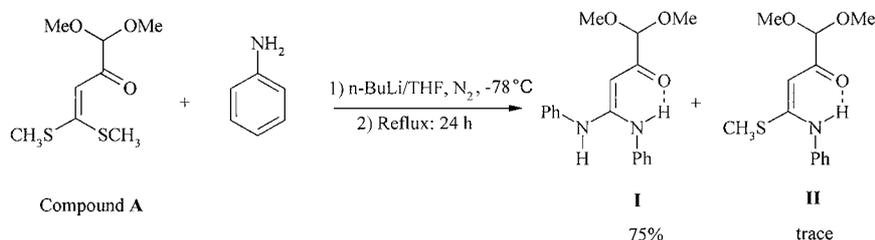


Fig. 1 Preparation of I by the reaction of α -oxoketene dithioacetal (compound A) and aniline.

Table 2 Fractional coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) of non-hydrogen atoms

Atom	x	y	z	U_{eq}
O(1)	3821(1)	178(1)	2259(1)	24(1)
O(2)	2974(1)	921(1)	3100(1)	22(1)
O(3)	3211(1)	1658(1)	1931(1)	22(1)
N(1)	3777(1)	385(1)	-883(2)	22(1)
N(2)	3996(1)	-240(1)	490(2)	20(1)
C(1)	3149(1)	1050(1)	-1946(2)	24(1)
C(2)	3052(1)	1596(1)	-2450(2)	27(1)
C(3)	3474(1)	2054(1)	-2349(2)	28(1)
C(4)	3993(1)	1961(1)	-1755(2)	29(1)
C(5)	4090(1)	1418(1)	-1260(2)	26(1)
C(6)	3668(1)	963(1)	-1354(2)	21(1)
C(7)	4655(1)	-671(1)	-721(2)	24(1)
C(8)	4897(1)	-1180(1)	-1147(2)	30(1)
C(9)	4729(1)	-1755(1)	-874(2)	34(1)
C(10)	4324(1)	-1825(1)	-153(2)	32(1)
C(11)	4083(1)	-1318(1)	281(2)	26(1)
C(12)	4239(1)	-741(1)	-10(2)	20(1)
C(13)	3804(1)	300(1)	109(2)	19(1)
C(14)	3617(1)	746(1)	778(2)	19(1)
C(15)	3632(1)	654(1)	1797(2)	19(1)
C(16)	3410(1)	1147(1)	2494(2)	20(1)
C(17)	3066(1)	2155(1)	2555(2)	30(1)
C(18)	2455(1)	697(1)	2538(2)	30(1)
O(4)	1161(1)	25(1)	5790(1)	21(1)
O(5)	1926(1)	688(1)	4713(1)	21(1)
O(6)	1845(1)	1479(1)	5859(1)	25(1)
N(3)	947(1)	-233(1)	7633(1)	17(1)
N(4)	1177(1)	499(1)	8862(2)	18(1)
C(19)	778(1)	-1286(1)	8008(2)	19(1)
C(20)	495(1)	-1742(1)	8510(2)	20(1)
C(21)	105(1)	-1593(1)	9220(2)	21(1)
C(22)	-10(1)	-987(1)	9412(2)	19(1)
C(23)	267(1)	-528(1)	8908(2)	17(1)
C(24)	671(1)	-679(1)	8214(2)	16(1)
C(25)	1018(1)	1603(1)	8870(2)	22(1)
C(26)	1179(1)	2174(1)	9221(2)	27(1)
C(27)	1667(1)	2245(1)	9894(2)	30(1)
C(28)	1991(1)	1742(1)	10226(2)	33(1)
C(29)	1834(1)	1169(1)	9870(2)	25(1)
C(30)	1349(1)	1097(1)	9192(2)	18(1)
C(31)	1152(1)	330(1)	7894(2)	17(1)
C(32)	1355(1)	706(1)	7139(2)	18(1)
C(33)	1347(1)	531(1)	6155(2)	16(1)
C(34)	1564(1)	977(1)	5380(2)	18(1)
C(35)	2016(1)	1925(1)	5159(2)	33(1)
C(36)	2481(1)	467(1)	5180(2)	32(1)

$$U_{\text{eq}} = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j^* (\mathbf{a}_i \cdot \mathbf{a}_j)$$

Two symmetrically independent molecules form two independent parallel polymeric chains in the crystal lattice via N-H...O hydrogen bonds (Table 4), which are connected to each other via weak C-H...O hydrogen bonds.

Table 3 Selected bond lengths (\AA) and angles (deg) for I

O(1)-C(15)	1.277(3)	O(6)-C(35)	1.431(2)
O(2)-C(16)	1.411(2)	N(1)-C(13)	1.347(3)
O(2)-C(18)	1.440(2)	N(1)-C(6)	1.434(3)
O(3)-C(16)	1.412(3)	N(2)-C(13)	1.354(3)
O(3)-C(17)	1.429(3)	N(2)-C(12)	1.418(3)
O(4)-C(33)	1.277(3)	N(3)-C(31)	1.358(3)
O(5)-C(34)	1.405(2)	N(3)-C(24)	1.425(3)
O(5)-C(36)	1.448(2)	N(4)-C(31)	1.353(3)
O(6)-C(34)	1.409(2)	N(4)-C(30)	1.433(3)
C(13)-C(14)	1.415(3)	C(14)-C(15)	1.386(3)
C(15)-C(16)	1.539(3)	C(33)-C(34)	1.536(3)
C(32)-C(33)	1.380(3)	C(31)-C(32)	1.412(3)
C(16)-O(2)-C(18)	112.99(16)	C(34)-O(5)-C(36)	113.32(17)
C(16)-O(3)-C(17)	111.68(18)	C(34)-O(6)-C(35)	111.52(17)
C(13)-N(1)-C(6)	123.9(2)	C(31)-N(3)-C(24)	129.7(2)
C(13)-N(2)-C(12)	128.6(2)	C(31)-N(4)-C(30)	123.01(19)

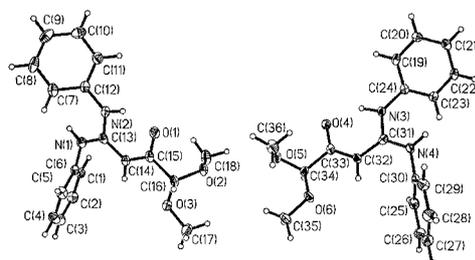


Fig. 2 Molecular structure of I (two symmetrically independent molecules), showing the atom-labeling scheme and 50% probability level displacement ellipsoids.

Table 4 Hydrogen bond D-H...A for I

D-H...A	d(D-H) \AA	d(H...A) \AA	d(D...A) \AA	$\angle \text{DHA}^\circ$
N(1)-H(1N)...O(1)#1	0.918(16)	1.951(19)	2.801(3)	153(2)
N(2)-H(2N)...O(1)	0.934(15)	1.785(18)	2.609(3)	145(2)
N(3)-H(3N)...O(4)	0.954(15)	1.775(18)	2.622(2)	146(2)
N(4)-H(4N)...O(4)#2	0.922(15)	1.979(17)	2.846(3)	156(2)

Symmetry transformation used to generate equivalent atoms:
#1 $x, -y, z - 1/2$, #2 $x, -y, z + 1/2$.

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