# Crystal structure of 3,3-diphenylnaphtho [1, 2-c] furan-1 (3H)-one

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The crystal structure of 3, 3-diphenylnaphtho[1, 2-c]furan-1(3H)-one **2** was determined by X-ray diffraction analysis. It possesses  $P_{2_1}2_12_1$  (#19) space group symmetry, with a = 11.922(2), b = 17.142(4), c = 8.429(2) Å, and  $D_{calc} = 1.297$  mg/m<sup>3</sup> for Z = 4.

KEY WORDS: Radical; single electron transfer; rearrangement; photosensitize.

# Introduction

The effect of homoconjugation on the reactivity of carbocations has long been known.<sup>1</sup> 7-diphenylmethylenebenzonorbonene 1 is a molecule in which there exists a homoconjugative interaction between the endocyclic and exocyclic olefinic double bonds. Recently, the reactions of electron-donor compounds with photoexcited acceptors resulting in electron transfer and the subsequent reactions (rearrangement, nucleophilic trapping of the cationic center by the solvent and trapping of the radical center by oxygen, etc.) of the donor cation radicals have received considerable attention.<sup>2</sup> As a result of the rapid development in the area of single electron transfer (SET) reactions of organic compounds, the phenomena of homoconjugation in organic cation radicals has also been recognized and investigations. Roth and his co-workers have provided evidence for the presence of homoconjugative interactions between nonconjugated olefinic double bonds (as in the cation radicals of 9-methylenebicyclo[4.2.1]nona-2, 4, 7-triene<sup>3a</sup> and 7-methylenenorbornadiene<sup>3b, 3c</sup>) and between an olefinic bond and a cyclopropane moiety (as in the cation radicals of 7-methylenequadricyclane<sup>3b, 3c</sup>

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and of norcaradiene<sup>3d</sup> systems). Ohashi and his coworkers have investigated the influence of homoconjugative interaction on the reactivity of cation radicals of 7-benzhydrylidenenorbornene derivatives.<sup>4</sup> In these investigations, the cation radicals have been generated by photoinduced single electron transfer (PET) processes, using cyano-substituted aromatics (such as 1,4-dicyano-benzene,<sup>3c,4</sup> 9, 10-dicyanoanthracene,<sup>3b</sup> etc.) or quinones (such as 2, 3, 5, 6-tetrachloro-1, 4-benzoquinone<sup>3a, 3b</sup>) as an electron acceptor sensitizer.

We report here an investigation on the reactivity of cation radicals of 7-diphenylmethylenenorbonene generated in PET reaction initiated by the electron acceptor sensitizer 2, 4, 6-tetraphenylpyrylium perchlorate (TPP<sup>+</sup>). The novel compound 3,3-diphenylnaphtho[1, 2-c]furan-1(3H)-one **2** was obtained by photoinduced electron transfer oxygenation of compound **1** (Scheme 1) and its MS, NMR, IR, and elemental analysis data are in accord with the assigned structure.



Scheme 1

Table 1. Crystal Data and Structure Refinement

CCDC-1003/5690	H13
colorless/prismatic	
$C_{24}H_{16}O_2$	C21 (
336.39	
293.1	,
orthorhombic	C.
$P2_{1}2_{1}2_{1}$ (#19)	H12
	0
	(
1722.4(6)	02 CI
4	
1.297	
0.81	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~
0.810	
Rigaku AFC7R/ $\omega$ -2 $\theta$ scans	113 09
13.7 - 21.2	
2274	
1878 $[I > 2\sigma(I)]$	
1878/0/236	
0.03	
93.59908	Сп
1.580	HIS
R1 = 0.0350, wR2 = 0.0420	
	CCDC-1003/5690 colorless/prismatic $C_{24}H_{16}O_{2}$ 336.39 293.1 orthorhombic $P2_{1}2_{1}2_{1}(\#19)$ 1722.4(6) 4 1.297 0.81 0.810 Rigaku AFC7R/ $\omega$ -2 $\theta$ scans 13.7 - 21.2 2274 1878 [ $I > 2\sigma(I)$ ] 1878/0/236 0.03 93.59908 1.580 R1 = 0.0350, wR2 = 0.0420



H14

Fig. 1. View of the title compound with displacement ellipsoids at the 50% probability level.

Atom	X	у	z	U(iso)
01	0.3173(1)	0.21621(8)	0.2240(2)	0.0480(4)
O2	0.4391(1)	0.11939(9)	0.1808(2)	0.0599(4)
C1	0.3642(2)	0.1600(1)	0.1312(3)	0.0448(5)
C2	0.3090(1)	0.1621(1)	-0.0245(2)	0.0402(5)
C3	0.2328(1)	0.2215(1)	-0.0242(2)	0.0420(5)
C4	0.2341(2)	0.2623(1)	0.1352(2)	0.0420(5)
C5	0.1641(2)	0.2354(1)	-0.1570(3)	0.0507(6)
C6	0.1758(2)	0.1873(1)	-0.2856(3)	0.0547(6)
C7	0.2553(2)	0.1260(1)	-0.2905(2)	0.0490(5)
C8	0.3263(2)	0.1127(1)	-0.1575(2)	0.0437(5)
C9	0.4078(2)	0.0532(1)	-0.1655(3)	0.0537(6)
C10	0.4190(2)	0.0098(1)	-0.3010(4)	0.0686(8)
C11	0.3491(2)	0.0219(2)	-0.4306(3)	0.0737(8)
C12	0.2683(2)	0.0781(2)	-0.4261(3)	0.0655(7)
C13	0.1241(2)	0.2555(1)	0.2264(2)	0.0436(5)
C14	0.1029(2)	0.3042(1)	0.3551(3)	0.0525(6)
C15	0.0070(2)	0.2951(1)	0.4454(3)	0.0563(6)
C16	-0.0695(2)	0.2377(1)	0.4084(3)	0.0581(7)
C17	-0.0517(2)	0.1904(1)	0.2789(3)	0.0647(7)
C18	0.0451(2)	0.1995(1)	0.1877(3)	0.0573(6)
C19	0.2774(2)	0.3463(1)	0.1243(2)	0.0468(5)
C20	0.3788(2)	0.3677(1)	0.1912(3)	0.0579(6)
C21	0.4149(2)	0.4451(2)	0.1847(4)	0.0757(8)
C22	0.3511(3)	0.4999(1)	0.1104(4)	0.0810(9)
C23	0.2514(3)	0.4793(1)	0.0421(4)	0.0844(9)
C24	0.2136(2)	0.4024(1)	0.0499(3)	0.0661(7)

Table 2. Table of Positional Parameters and Their Estimated Standard Deviations

# 3,3-diphenylnaphtho [1,2-c] furan-1(3H)-one

# **Experimental**

A solution of 0.612 g 7-diphenylmethylenebenzonorbornene **1** (2.0 mmol) in 40 mL CH<sub>2</sub>Cl<sub>2</sub> was photolyzed with TPP<sup>+</sup> as sensitizer. The solution was then irradiated with light  $\lambda > 400$  nm at room temperature under continuous dry oxygen purging. At the end of the reaction (TLC monitoring), the solvent was removed *in vacuo* and the residue was separated by flash chromatography on a silica gel column with petroleum ether (b.p. 60-90°C)-ethyl acetate (10:1) as eluents to give the title compound **2** (200 mg at yield 30%). Clear, colorless single crystals suitable for X-ray diffraction analysis were obtained from ethyl acetate solution.

All measurements were made on a Rigaku AFC7R diffractometer with graphite monochromated Mo- $K\alpha$  radiation. The data were corrected for Lorentz and polarization. The structure was solved by direct methods<sup>5</sup> and expanded using Fourier techniques.<sup>6</sup> Refinement was by full-matrix least-squares methods with anisotropic displacement parameters for all non-H-atoms and isotropic displacement parameters for H atoms. All calculations were performed using the teXsan<sup>7</sup> crystallographic software package of Molecular Structure Corporation. A summary of crystal data and structure refinement is provided in Table 1, the refined atomic coordinates are given in Table 2.

# Spectroscopic data

Colorless prisms, m.p. 168°C,  $\nu_{max}/cm^{-1}$  3050, 1740, 1580, 1490, 1445, 1200, 1180, 1120, 955, 827, 783, 755, 700;  $\delta_{\rm H}/{\rm ppm}$  (500 MHz, CDCl<sub>3</sub>) 7.32–7.38 (10H, m, ArH); 7.59–7.63 (2H, m, ArH), 7.72 (1H, t, *J* 7.5, ArH), 7.93 (1H, d, *J* 8.2, ArH), 8.11 (1H, d, *J* 8.2, ArH), 9.07 (1H, d, *J* 8.2, ArH); *m/z*(%) 336 (M<sup>+</sup>, 33), 259 (72), 231 (100), 165 (6). (Found: C, 85.60; H, 4.91. C<sub>24</sub> H<sub>16</sub>O<sub>2</sub> requires C, 85.71; H, 4.76).

#### **Results and discussion**

Figure 1 shows the ORTEP drawing of the title compound **2** with the atom-numbering scheme. Positional parameters and their estimated standard deviations are listed in Table 2. Selected bond lengths and angles are listed in Table 3. The five atoms forming the heterocyclic furanone ring all lie in the same plane. The torsion angles C1-O1-C4-C3 and

 
 Table 3. Selected Bond Distance (Å) and Angles (°) with esd's in Parentheses

O1-C1	1.361(2)	C1-C2-C3	108.3(2)
O1-C4	1.472(2)	C1-C2-C8	128.8(2)
O2-C1	1.207(2)	C3-C2-C8	122.9(2)
C1-C2	1.469(3)	C2-C3-C4	109.8(2)
C2-C3	1.365(3)	C2-C3-C5	120.9(2)
C3-C4	1.515(3)	C4-C3-C5	129.3(2)
C4-C13	1.523(3)	O1-C4-C3	102.1(1)
C4-C19	1.533(3)	O1-C4-C13	106.4(1)
C1-O1-C4	111.4(1)	O1-C4-C19	107.9(2)
O1-C1-O2	120.9(2)	C3-C4-C13	113.8(2)
O1-C1-C2	108.2(2)	C3-C4-C19	112.6(2)
O2-C1-C2	130.9(2)	C13-C4-C19	113.1(2)

O1-C4-C3-C2 are 3.5(2) and  $-2.0(2)^\circ$ , respectively, meanwhile, the largest deviation being 0.023(2) Å for the C1 atom. The O2 atom lies 0.083 Å above this plane. The C1=O2 bond distance of 1.207(2) Å (Table 3) agrees well with those in related compounds<sup>8</sup> and with the value for a C=O double bond (1.202 Å) reported by Allen *et al.*<sup>9</sup> The bond lengths of 1.361 (2) Å for O1-C1 and 1.472(2) Å for O1-C4 indicate that the former is a O-C(=O) single bond and the later is a (C-)C-O single bond.<sup>9</sup> In the naphtho [1,2-c]furan framework of the molecule, the three fused rings are in a plane within estimated limits of error.

The dihedral angles between rings A and B, A and C, A and D, B and C, B and D, and C and D are 3.74, 104.89, 61.24, 108.27, 59.55, and 99.26°, respectively. The plane A and plane B are nearly coplanar with a small dihedral angle of 3.74°. Plane C and plane D are almost perpendicular to each other with a dihedral angle of 99.26° in order to minimize the steric hindrance between the H-atoms on the two benzene rings.

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