Supporting Information for the Paper:

Photochemical Ring Opening of 7-Benzoyl- and 7-Methoxycarbonyldibenzonorcaradienes. Competing 1,2-Hydrogen Shift and Cyclization Reactions of 1,3-Diradicals.

by Aneta Bogdanova and Vladimir V. Popik

Experimental Section

General Methods. ^{1}H NMR and ^{13}C spectra were recorded on either Varian Gemini-200 or Varian Unity Plus-400 NMR spectrometers. All NMR spectra were recorded in $CDCl_3$ solutions and chemical shifts are reported in ppm relative to TMS. UV/vis spectra were acquired on a Cary 50 UV/vis spectrophotometer. IR spectra were recorded in CCl_4 solutions using Mattson Galaxy 6020 FT-IR instrument. Solvents were distilled prior to use: THF from sodium/benzophenone ketyl, methylene chloride from phosphorus pentoxide, and methanol from sodium methoxide. Methyl 2-diazo-2-phenylacetate[1] and benzoyl diazomethane[2] were prepared according to literature procedures. All other chemicals were used as received from commercial suppliers. Photolyses were carried out using Rayonet photoreactor equipped with eight RMR 3000 mercury lamps (λ_{Emiss}= 300 nm). Analysis of reaction mixtures was conducted using Shimadzu HPLC instrument equipped with 30 cm Supelco Discovery C-18 column and methanol/water mixtures as an eluant. Pure samples of **1a-1c** and **2a,b** served as a reference. The preparative photolyses of **1a** and **1b** are described below.

General procedure for preparation of dibenzonorcaradienes 1a and 1b.
110 mg of rhodium (II) octanoate dimer were added to the vigorously stirred solution of 4.45 g (25 mM) of phenanthrene in 30 mL of methylene chloride under argon. The reaction mixture was brought to reflux and 5 mM of diazocompound in 20 mL of methylene chloride was added dropwise over 2 h. Solvent was removed in vacuum at room temperature and dibenzonorcaradiene was isolated by flash chromatography on silica gel (hexane:CH_2Cl_2) and recrystallized from acetone.
It is noteworthy that the major byproduct isolated from the above procedure was dimer of the corresponding α-carbonylcarbene.

7-Methoxycarbonyl-7-phenyldibenzonorcaradiene (1a): colorless crystals; m.p. 235^{0}C; ^{1}H NMR, δ: 7.54 – 6.35 (13H, m), 3.67 (2H, s), 3.61 (3H, s); ^{13}C NMR, δ: 174.8, 131.7, 130.3, 129.9, 129.4, 126.6, 126.1, 125.9, 125.6, 125.2, 121.4, 51.8, 34.3, 30.6; IR, cm^{-1}: 2960 (m), 1739 (vs), 1260 (s), 1016 (vs); UV (methanol), nm/log(ε): 271/4.2, 299/3.8, 311/3.8; MS, m/z (%): 326 (21), 294 (32), 265(100) 132 (70)

***trans*-7-Benzoyldibenzonorcaradiene (1b)**: colorless crystals; m.p. 221-224^{0}C; ^{1}H NMR, δ: 7.99 (4H, dd, J = 7.2 Hz), 7.58-7.31 (9H, m), 3.53 (2H, d, J=3.6 Hz), 2.12 (1H, t, J=3.6 Hz); ^{13}C NMR, δ: 199.8, 159.2, 136.8, 133.6, 132.9, 129.8, 128.5, 128.1, 127.3, 123.3, 33.7, 31.2; UV (methanol), nm/log(ε): 233/4.2, 241/4.2, 270/4.3, 299/3.9, 311/3.8; MS, m/z (%): 296 (91), 191 (97), 189 (42), 165 (29), 105 (100), 77 (64).

Preparative photolysis of 7-methoxycarbonyl-7-phenyldibenzonorcaradienes 1a.
37 mg (0.113 mM) of **1a** were dissolved in 15 mL of methanol : THF mixture (1:1) and irradiated for 14 h. The product was isolated from reaction mixture by flash chromatography on silica gel (hexanes : methylene chloride) to give 12.4 mg of pure **2a**.

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[1] Starmans, W.A. J.; Thijs, L.; Zwanenburg, B.; *Tetrahedron*, **1998**, *54*, 629.
[2] Yates, P.; Garneau, F. X.; Lokensgard, J. P. *Tetrahedron* **1975**, *31*, 1979.

2-(9-Phenanthryl)-phenylacetate 2a. colorless crystals, m.p. 65^{0}C; ^{1}H NMR, δ: 7.17-8.67 (14H, m), 5.72 (1H, s), 3.71 (3H, s); ^{13}C NMR, δ: 173.2, 137.6, 137.7, 131.3, 130.9, 130.7, 130.1, 129.1, 128.9, 128.7, 127.5, 127.4, 127.0, 126.9, 126.8, 126.5, 123.9, 123.3, 122.4, 54.0, 52.6; IR, cm^{-1}: 2928 (s), 1743 (vs), 1454 (s), 1154 (m), 1030(s); UV (methanol), nm/log(ε): 254/5.0, 276/4.3, 296/4.3; MS, m/z (%): 326 (38), 265 (100), 132 (28), 59 (33).

Preparative photolysis of *trans*-7-benzoyldibenzonorcaradiene 1b.
100 mg (0.306 mM) of **1a** were dissolved in 15 mL of methanol and irradiated at 300 nm for 45 min (about 60% conversion by HPLC). The reaction mixture was separated by flash chromatography on silica gel (hexanes : methylene chloride) providing 32 mg of **2b**, 19 mg of starting material (**1b**), and 12 mg of **1c** in addition to 18 mg of mixed fraction (**1b** + **1c**).

***cis*-7-Benzoyldibenzonorcaradiene (1c)**: colorless crystals, m.p. 162-165^{0}C; ^{1}H NMR, δ: 7.93 (4H, dd, J =8.0 Hz), 7.45-7.24 (9H, m), 3.40 (2H, d, J=9.1), 3.21 (1H, t, J=9.1 Hz); ^{13}C NMR, δ: 194.0; 138.7, 132.6, 132.2, 130.1, 130.0, 128.2, 127.8, 127.5, 127.1, 122.5, 28.9, 21.6; UV (methanol), nm/log(ε): 232/4.0, 242/3.9, 271/3.9, 298/3.5, 309/3.4; MS, m/z (%): 296 (87), 191 (100), 189 (40), 165 (36), 105 (84), 77 (47).

ω-(9-Phenanthryl)acetophenone (2b)[3]: colorless crystals, m.p. 151-153^{0}C; ^{1}H NMR, δ: 8.78 (2H, dd, J =4.0/15.2 Hz), 8.11-7.20 (13H, m), 4.76 (2H, s); ^{13}C NMR, δ: 197.7, 136.7, 133.3, 131.6, 131.2, 130.8, 130.0, 129.9, 128.8, 128.7, 128.5, 128.3, 126.8, 126.7, 126.5, 126.4, 124.5, 123.2, 122.5, 28.9; UV (methanol), nm/log(ε): 252/4.5, 276/4.2, 296/3.9, 311/3.7; MS, m/z (%): 296 (32), 191 (24), 105 (100), 77 (37).

UV Spectra of photolysis of 1a and 1b

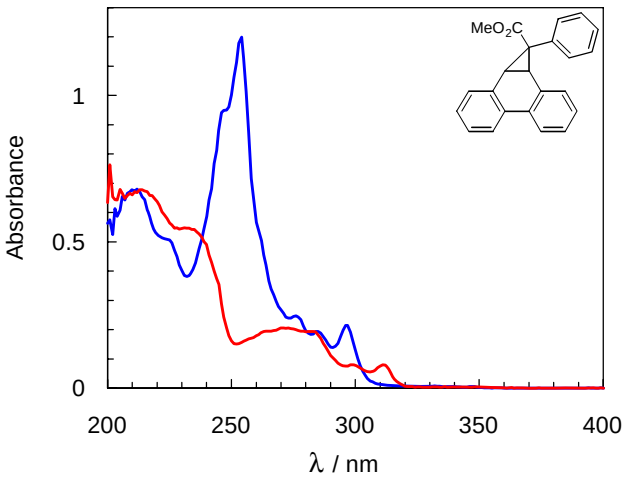

Figure 1. 5*10^{-5} M solution of **1a** in methanol (red line); after 20 min irradiation at 300 nm (blue line).

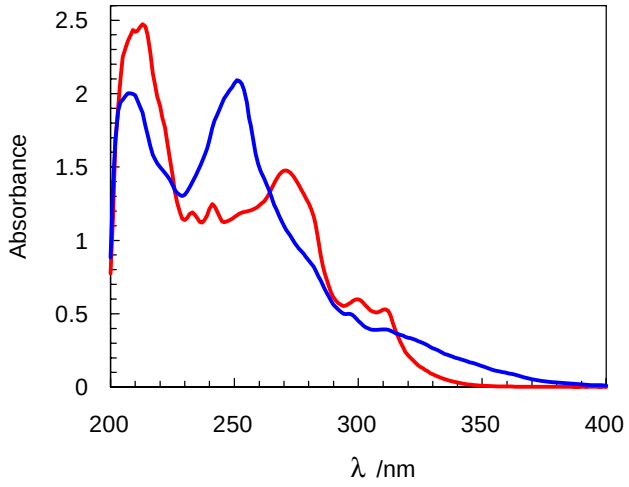

Figure 2. 5*10^{-5} M solution of **1b** in methanol (red line); after 5 min of irradiation at 300 nm (blue line).

[3] Katz, J.T.; Sivavac,T.M. *J.Am.Chem.Soc.*, **1985**, *107*, 737.

X-ray data for 1b

Table 1. Crystal data and structure refinement for k0029.

Identification code	k0029	
Empirical formula	C22 H16 O	
Formula weight	296.35	
Temperature	150(1) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)	
Unit cell dimensions	a = 8.0301(12) Å	α= 90°.
	b = 5.5328(9) Å	β= 97.373(8)°.
	c = 16.719(2) Å	γ = 90°.
Volume	736.67(19) $Å^3$	
Z	2	
Density (calculated)	1.336 Mg/m^3	
Absorption coefficient	0.080 mm^{-1}	
F(000)	312	
Crystal size	0.35 x 0.10 x 0.07 mm^3	
Theta range for data collection	2.56 to 25.03°.	
Index ranges	0<=h<=9, 0<=k<=6, -19<=l<=19	
Reflections collected	7832	
Independent reflections	1432 [R(int) = 0.0000]	
Completeness to theta = 25.03°	98.6 %	
Absorption correction	multi-scan (Denzo-SMN)	
Max. and min. transmission	0.9944 and 0.9725	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	1432 / 1 / 209	
Goodness-of-fit on F^2	1.023	
Final R indices [I>2sigma(I)]	R1 = 0.0650, wR2 = 0.1337	
R indices (all data)	R1 = 0.1031, wR2 = 0.1521	
Extinction coefficient	0.008(10)	
Largest diff. peak and hole	0.239 and -0.240 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for k0029. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	8365(4)	5281(7)	3166(2)	43(1)
C(1)	9182(6)	1341(9)	2871(2)	33(1)
C(2)	8957(6)	1963(9)	1966(2)	34(1)
C(3)	8670(6)	17(10)	1368(2)	35(1)
C(4)	7105(6)	-75(11)	887(3)	41(1)
C(5)	6733(7)	-1878(11)	317(3)	45(2)
C(6)	7948(7)	-3546(11)	212(3)	44(2)
C(7)	9496(7)	-3522(9)	679(3)	39(1)
C(8)	9894(6)	-1707(9)	1261(2)	34(1)
C(9)	11591(6)	-1550(9)	1746(2)	32(1)

C(10)	12852(6)	-3210(9)	1654(3)	38(1)
C(11)	14457(6)	-2961(10)	2078(3)	41(1)
C(12)	14820(6)	-1015(11)	2585(3)	44(2)
C(13)	13607(6)	630(11)	2684(3)	39(1)
C(14)	11956(6)	386(10)	2282(2)	33(1)
C(15)	10669(6)	2179(9)	2440(3)	34(1)
C(16)	8502(6)	3162(10)	3384(3)	32(1)
C(17)	7945(6)	2416(9)	4181(3)	31(1)
C(18)	6970(6)	4061(11)	4543(3)	38(1)
C(19)	6535(7)	3587(10)	5305(3)	40(1)
C(20)	7100(6)	1505(10)	5707(3)	38(1)
C(21)	8045(6)	-138(11)	5344(3)	40(1)
C(22)	8478(6)	299(10)	4572(2)	32(1)

Table 3. Bond lengths [Å] and angles [°] for k0029.

O(1)-C(16)	1.228(6)
C(1)-C(16)	1.472(7)
C(1)-C(2)	1.541(6)
C(1)-C(15)	1.543(6)
C(2)-C(3)	1.467(7)
C(2)-C(15)	1.501(6)
C(3)-C(8)	1.397(7)
C(3)-C(4)	1.403(7)
C(4)-C(5)	1.386(7)
C(5)-C(6)	1.370(8)
C(6)-C(7)	1.381(7)
C(7)-C(8)	1.407(7)
C(8)-C(9)	1.496(6)
C(9)-C(10)	1.390(7)
C(9)-C(14)	1.403(7)
C(10)-C(11)	1.396(7)
C(11)-C(12)	1.378(8)
C(12)-C(13)	1.359(7)
C(13)-C(14)	1.414(6)
C(14)-C(15)	1.481(7)
C(16)-C(17)	1.518(6)
C(17)-C(22)	1.382(7)
C(17)-C(18)	1.388(7)
C(18)-C(19)	1.389(7)
C(19)-C(20)	1.381(7)
C(20)-C(21)	1.375(7)
C(21)-C(22)	1.400(6)

C(16)-C(1)-C(2)	114.4(4)
C(16)-C(1)-C(15)	115.7(4)
C(2)-C(1)-C(15)	58.3(3)

C(3)-C(2)-C(15)	118.2(4)
C(3)-C(2)-C(1)	119.6(4)
C(15)-C(2)-C(1)	60.9(3)
C(8)-C(3)-C(4)	119.6(5)
C(8)-C(3)-C(2)	122.4(4)
C(4)-C(3)-C(2)	117.9(5)
C(5)-C(4)-C(3)	121.3(5)
C(6)-C(5)-C(4)	118.6(5)
C(5)-C(6)-C(7)	121.7(5)
C(6)-C(7)-C(8)	120.4(5)
C(3)-C(8)-C(7)	118.4(4)
C(3)-C(8)-C(9)	119.9(4)
C(7)-C(8)-C(9)	121.7(5)
C(10)-C(9)-C(14)	118.7(4)
C(10)-C(9)-C(8)	121.9(4)
C(14)-C(9)-C(8)	119.4(4)
C(9)-C(10)-C(11)	121.1(5)
C(12)-C(11)-C(10)	119.9(5)
C(13)-C(12)-C(11)	120.0(5)
C(12)-C(13)-C(14)	121.4(5)
C(9)-C(14)-C(13)	118.9(5)
C(9)-C(14)-C(15)	122.2(4)
C(13)-C(14)-C(15)	118.9(5)
C(14)-C(15)-C(2)	117.7(4)
C(14)-C(15)-C(1)	118.8(4)
C(2)-C(15)-C(1)	60.8(3)
O(1)-C(16)-C(1)	120.5(4)
O(1)-C(16)-C(17)	119.6(4)
C(1)-C(16)-C(17)	119.9(5)
C(22)-C(17)-C(18)	120.5(4)
C(22)-C(17)-C(16)	122.5(5)
C(18)-C(17)-C(16)	116.8(4)
C(17)-C(18)-C(19)	119.8(5)
C(20)-C(19)-C(18)	119.9(5)
C(21)-C(20)-C(19)	120.1(4)
C(20)-C(21)-C(22)	120.7(5)
C(17)-C(22)-C(21)	118.9(5)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for k0029. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	52(2)	43(2)	33(2)	5(2)	2(2)	4(2)
C(1)	37(3)	36(3)	26(2)	1(2)	1(2)	-1(2)
C(2)	36(3)	38(3)	26(2)	7(3)	-1(2)	4(3)
C(3)	43(3)	39(3)	24(2)	7(3)	3(2)	-6(3)

C(4)	40(3)	50(4)	31(2)	7(3)	-1(2)	4(3)
C(5)	40(3)	56(4)	37(3)	-5(3)	1(2)	-10(3)
C(6)	49(3)	58(4)	25(2)	-7(3)	2(2)	-13(3)
C(7)	49(3)	35(3)	31(3)	-6(3)	5(2)	-5(3)
C(8)	44(3)	36(3)	21(2)	5(3)	6(2)	-2(3)
C(9)	39(3)	36(3)	21(2)	6(3)	3(2)	-4(3)
C(10)	41(3)	40(3)	32(3)	-2(3)	7(2)	1(3)
C(11)	39(3)	47(4)	39(3)	7(3)	12(2)	10(3)
C(12)	32(3)	61(4)	38(3)	5(3)	1(2)	-1(3)
C(13)	39(3)	47(3)	32(2)	3(3)	7(2)	-4(3)
C(14)	27(3)	46(3)	25(2)	9(3)	4(2)	-1(3)
C(15)	35(3)	36(3)	30(2)	-5(2)	2(2)	-7(2)
C(16)	31(3)	34(3)	30(2)	4(3)	-1(2)	5(2)
C(17)	24(3)	39(3)	27(2)	-2(2)	-2(2)	-5(2)
C(18)	37(3)	40(3)	37(3)	5(3)	1(2)	7(3)
C(19)	46(3)	40(4)	34(3)	-4(3)	11(2)	8(3)
C(20)	37(3)	47(4)	30(3)	-3(3)	6(2)	-1(3)
C(21)	38(3)	47(4)	32(3)	1(3)	-1(2)	-2(3)
C(22)	35(3)	31(3)	29(2)	-2(3)	-3(2)	-5(2)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for k0029.

	x	y	z	U(eq)
H(1A)	9132	-397	3031	40
H(2A)	8372	3524	1814	40
H(4A)	6285	1121	953	49
H(5A)	5659	-1956	5	54
H(6A)	7719	-4750	-192	53
H(7A)	10298	-4739	607	46
H(10A)	12617	-4538	1297	45
H(11A)	15298	-4130	2017	49
H(12A)	15918	-823	2865	52
H(13A)	13873	1972	3032	47
H(15A)	11081	3861	2563	40
H(18A)	6602	5508	4269	46
H(19A)	5849	4693	5549	48
H(20A)	6836	1208	6236	45
H(21A)	8407	-1584	5619	48
H(22A)	9127	-842	4321	39