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Natural Polyprenylated Benzophenones: Keto-Enol Tautomerism and Stereochemistry

Felipe T. Martins,[a] José W. Cruz Jr.,[a] Priscilla B. M. C. Derogis,[b] Marcelo H. dos Santos,[b] Márcia P. Veloso,[b] Javier Ellena[c] and Antônio C. Doriguetto*[,a]

[a]Laboratório de Cristalografia and [b]Laboratório de Fitoquímica e Química Medicinal, Departamento de Ciências Exatas, Universidade Federal de Alfenas, 37130-000 Alfenas-MG, Brazil

[c]Instituto de Física de São Carlos, Universidade de São Paulo, CP 369, 13560-970 São Carlos-SP, Brazil

Supplementary crystallographic data sets for (**a**) are available through the Cambridge Structural Data Base, deposition number CCDC 643597. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44123-336-033; e-mail: deposit@ccdc.cam.ac.uk or http:www.ccdc.ac.uk)

*Guttiferone A (**a**)*

Yellow crystalline solid, mp 120-123 °C (MeOH). $[\alpha]_D$ = +47.6° (c1.00,$CHCl_3$); IR (KBr) ν_{max}/cm^{-1}: 3450, 1730, 1670, 1600. UV (MeOH, 0.1 %) λ_{max}/nm: 228, 280. IE/MS *m/z* (%): 602 (1), 533 (22), 341 (42), 231 (34), 189 (9), 137 (26), 109 (11), 69 (100). The NMR data are as follows: ^{1}H NMR (400 MHz, pyridine-d_5) δ_H 7.87 (1H, *d*, *J* 2.1 Hz, H-12), 7.61 (1H, *dd*, *J* 2.1 and 8.3 Hz, H-16), 7.41 (1H, *d*, *J* 8.3 Hz, H-15), 5.76 (1H, *m*, H-20), 5.56 (1H, *m*, H-30), 5.20 (1H, *m*, H-25 and H-35), 3.04 (2H, *m*, H_2-24), 2.92 (2H, *m*, H_2-19 and H_2-29), 2.60 (2H, *m*, H_2-8b), 2.48 (2H, *d*, *J* 14.2 Hz, H_2-8a; *m*, H_2-8b), 2.33 (2H, *dd*, *J* 2.3 and 14.2 Hz, H_2-8a), 2.06 (1H, *m*, H-7), 2.06 (2H, *m*, H_2-34), 2.00 (2H, *m*, H_2-18), 1.79-1.59 (3H, *m*, H_3-22, H_3-23, H_3-27, H_3-28, H_3-32, H_3-33, H_3-37 and H_3-38), 1.52 (3H, *s*, H_3-17a), 1.01 (3H, *s*, H_3-17b); ^{13}C NMR (100 MHz, pyridine-d_5) δ_C 210.1 (C-9a), 201.7 (C-9b), 196.3 (C-10b), 195.9 (C-10a), 191.7 (C-2), 191.2 (C-4a), 191.1 (C-4b), 153.5 (C-14a), 147.2 (C-13b), 147.2 (C-13a), 143.1 (C-14b), 134.0 (C-31a), 133.8 (C-21a), 133.7 (C-21b), 133.4 (C-31b), 132.7 (C-26a), 132.1 (C-36a), 131.5 (C-26b), 131.2 (C-36b), 130.5 (C-11), 126.3 (CH-35a), 125.8 (CH-35b), 125.1 (CH-25a), 124.4 (CH-16a), 124.1 (CH-16b), 123.7 (CH-25b), 122.1 (CH-30), 121.8 (CH-20b), 121.0 (CH-20a), 119.0 (C-3), 117.5 (CH-12), 115.8 (CH-15a), 115.7 (CH-15b), 69.2 (C-5b), 62.9 (C-1b), 68.1 (C-5a), 61.2 (C–1a), 50.5 (C-6a), 49.8 (C-6b), 41.8 (CH_2-8b), 40.8 (CH-7b), 40.7 (CH-7a), 38.7 (CH_2-8a), 37.0 (CH_2-18b), 36.6 (CH_2-18a), 31.7 (CH_2-29a), 31.5 (CH_2-29b), 29.9 (CH_2-19), 26.5 (CH_2-24b), 26.4 (CH_2-24a), 26.3 (CH_3-27a), 26.3 (CH_3-27b), 26.1 (CH_3-23 and CH_3-33), 26.0 (CH_3-38a), 26.0 (CH_3-38b), 24.8 (CH_2-34b), 23.3 (CH_2-34a), 19.9 (CH_3-17a), 18.7 (CH_3-32), 18.6 (CH_3-28b), 18.5 (CH_3-28a), 18.5 (CH_3-22a), 18.4 (CH_3-22b), 18.2 (CH_3-37b), 17.9 (CH_3-37a), 16.5 (CH_3-17b).

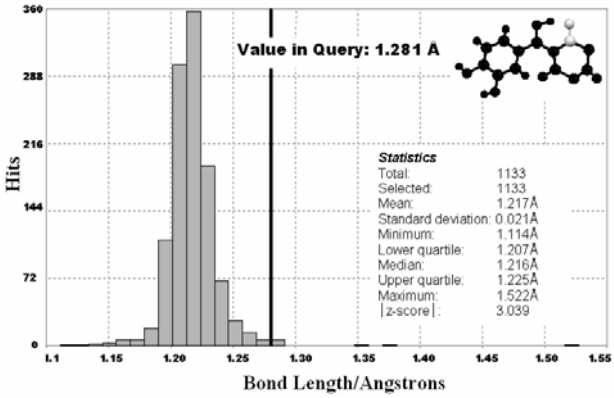

Figure S1. Histogram comparing the C4=O1 bond length with the C=O bond lengths in CSD entries containing structures similar to (**a**).

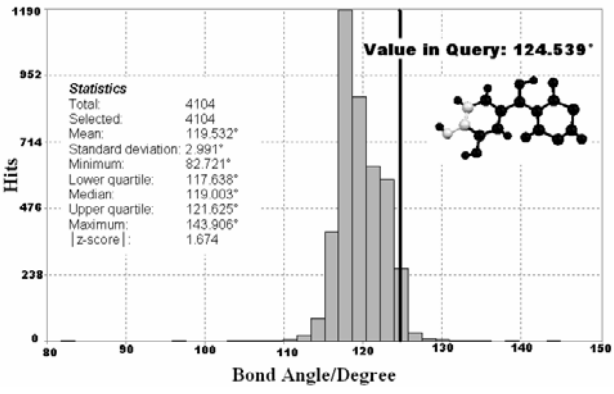

Figure S2. Histogram comparing the O6-C14–C13 bond angle with the O-C-C bond angles in CSD entries containing structures similar to (**a**).

*e-mail: doriguetto@unifal-mg.edu.br

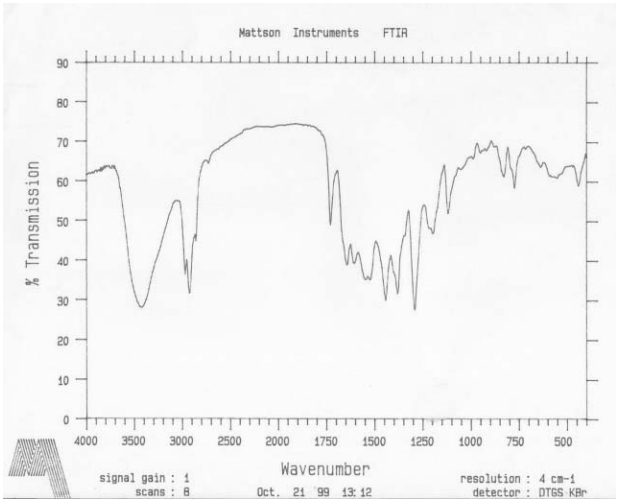

Figure S3. Infrared spectrum (KBr).

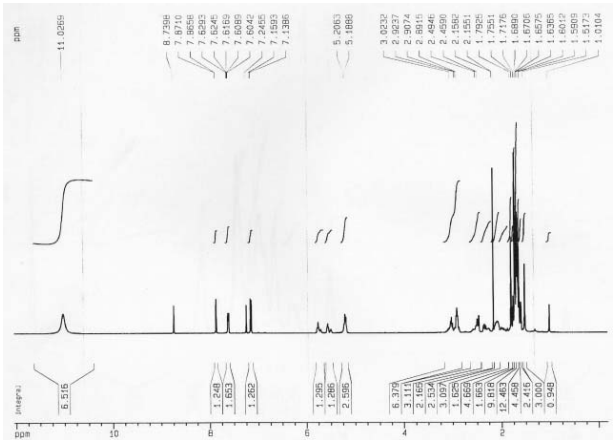

Figure S6. ^{1}H NMR spectrum (400 MHz, pyridine-d_5).

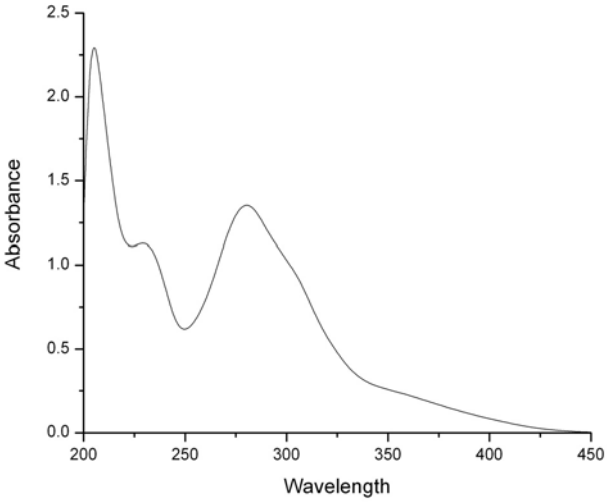

Figure S4. UV spectrum (MeOH, 0.1 %).

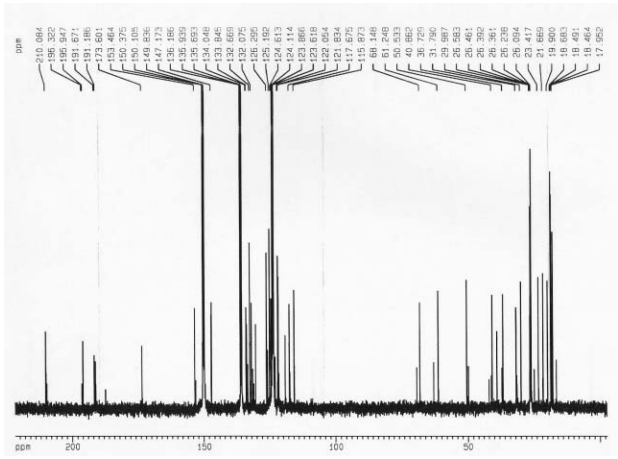

Figure S7. ^{13}C NMR spectrum (100 MHz, pyridine-d_5).

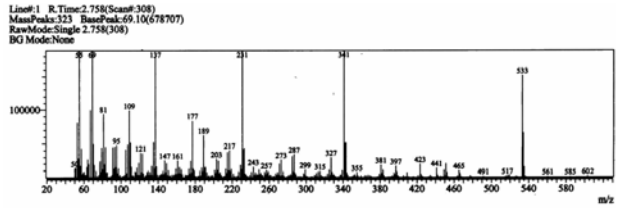

Figure S5. Electron impact mass spectrum.

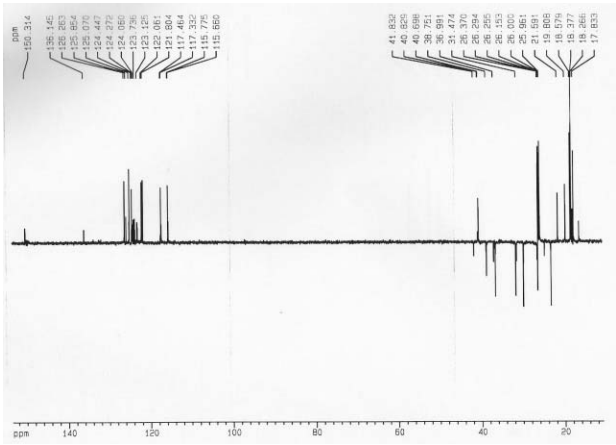

Figure S8. ^{13}C 135-DEPT NMR spectrum (100 MHz, pyridine-d_5).

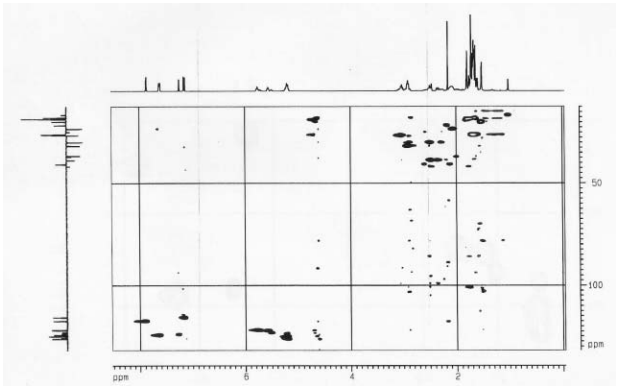

Figure S9. HMQC spectrum (400 and 100 MHz, pyridine-d_5).

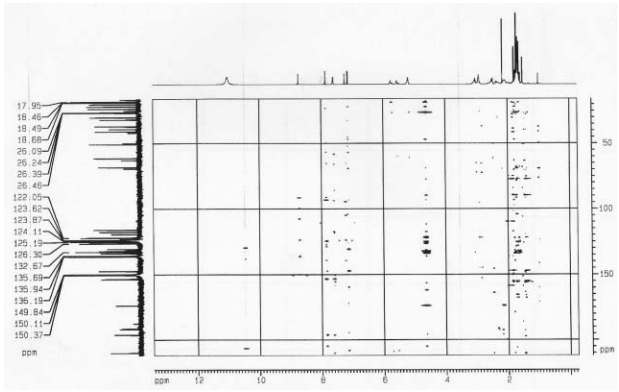

Figure S10. HMBC spectrum (400 and 100 MHz, pyridine-d_5).

Table S1. Bond lengths in Å for (**a**) determined by XRD (query value) and MOGUL intramolecular analysis

Bond	Hits	Mean	Query value
C1-C2	7	1.516 (2)	1.515 (5)
C2-C3	94	1.447 (3)	1.457 (5)
C3-C4	94	1.447 (3)	1.416 (5)
C4-C5	4	1.538 (2)	1.528 (5)
C5-C6	5	1.586 (2)	1.615 (5)
C6-C7	27	1.566 (4)	1.579 (5)
C7-C8	249	1.535 (2)	1.534 (5)
C1-C8	58	1.538 (2)	1.556 (5)
C1-C9	31	1.508 (4)	1.497 (5)
C1-C29	62	1.561 (5)	1.555 (5)
C3-C10	9	1.380 (1)	1.413 (5)
C5-C9	4	1.526 (2)	1.503 (5)
C5-C19	3	1.545 (5)	1.555 (5)
C6-C17	2438	1.537 (2)	1.526 (6)
C6-C18	18	1.550 (1)	1.551 (5)
C7-C24	22	1.545 (1)	1.538 (5)
C10-C11	44	1.481 (1)	1.469 (6)
C11-C12	10000	1.388 (2)	1.392 (6)
C11-C16	7743	1.390 (2)	1.392 (6)
C12-C13	10000	1.383 (2)	1.368 (6)
C13-C14	4105	1.391 (2)	1.363 (6)
C14-C15	216	1.395 (2)	1.389 (6)
C15-C16	2565	1.384 (2)	1.368 (6)
C18-C34	182	1.530 (4)	1.521 (6)
C19-C20	138	1.494 (3)	1.501(6)
C20-C21	334	1.315 (4)	1.309 (6)
C21-C22	1038	1.497 (3)	1.486 (7)
C21-C23	1038	1.497 (3)	1.513 (7)
C24-C25	160	1.497 (2)	1.485 (6)
C25-C26	334	1.315 (4)	1.316 (7)
C26-C27	1038	1.497 (3)	1.503 (7)
C26-C28	1038	1.497 (3)	1.514 (9)
C29-C30	138	1494 (3)	1.496 (7)
C30-C31	334	1.315 (4)	1.306 (8)
C31-C32	1038	1.497 (3)	1.535 (9)
C31-C33	1038	1.497 (3)	1.496 (9)
C34-C35	558	1.501 (3)	1.497 (7)
C35-C36	334	1.315 (4)	1.311 (7)
C36-C37	1038	1.497 (3)	1.468 (9)
C36-C38	1038	1.497 (3)	1.506 (8)
O1-C4	1133	1.217 (2)	1.281 (4)
O2-C10	155	1.329 (3)	1.297 (5)
O3-C2	1133	1.217 (2)	1.239 (4)
O4-C9	846	1.205 (2)	1.221 (5)
O5-C15	6759	1.362 (2)	1.372 (6)
O6-C14	6759	1.362 (2)	1.365 (5)

Table S2. Bond Angle (°) for (**a**) determined by XRD (query value) and MOGUL intramolecular analysis

Angle	Hits	Mean	Query value	Angle	Hits	Mean	Query value
C1-C2-C3	2	119 (2)	119.51 (3)	C11-C16-C15	85	119 (1)	119.66 (4)
C1-C8-C7	7	114 (1)	115.61 (3)	C12-C11-C16	2285	119 (2)	118.45 (4)
C1-C9-C5	3	114 (1)	114.83 (3)	C12-C13-C14	1329	120 (1)	119.97 (4)
C1-C2-C30	27	113 (2)	113.83 (3)	C13-C14-C15	169	119 (2)	119.55 (4)
C2-C1-C8	15	108 (2)	108.85 (3)	C14-C15-C16	218	119 (1)	120.99 (4)
C2-C1-C9	3	106 (4)	111.49 (3)	C17-C6-C18	12	108 (3)	107.78 (3)
C2-C1-C29	9	109 (2)	108.81 (3)	C18-C34-C35	150	113 (3)	112.96 (3)
C2-C3-C4	22	119 (1)	116.53 (3)	C19-C20-C21	68	128 (4)	128.24 (3)
C2-C3-C10	20	119 (2)	123.80 (3)	C20-C21-C22	668	122 (4)	124.23 (3)
C3-C4-C5	21	118 (3)	123.29 (3)	C20-C21-C23	668	122 (4)	121.62 (3)
C3-C10-C11	7	127 (1)	126.86 (3)	C22-C21-C23	519	114 (3)	114.14 (3)
C4-C3-C10	20	119 (2)	117.90 (3)	C24-C25-C26	24	128 (2)	130.66 (5)
C4-C5-C6	12	109 (3)	111.50 (3)	C25-C26-C27	668	122 (4)	121.57 (5)
C4-C5-C9	2	110 (1)	108.00 (3)	C25-C26-C28	668	122 (4)	123.12 (5)
C4-C5-C19	2	108 (1)	106.66 (3)	C27-C26-C28	519	114 (3)	115.31 (5)
C5-C6-C7	15	109 (3)	110.10 (3)	C29-C30-C31	68	128 (4)	127.79 (5)
C5-C6-C17	5	108 (1)	111.44 (3)	C30-C31-C32	668	122 (4)	121.71 (5)
C5-C6-C18	15	112 (2)	107.70 (3)	C30-C31-C33	668	122 (4)	125.55 (5)
C5-C19-C20	3	113 (1)	111.96 (3)	C32-C31-C33	519	114 (3)	112.68 (5)
C6-C5-C9	16	109 (4)	106.00 (3)	C34-C35-C36	109	127 (4)	128.95 (5)
C6-C5-C19	15	113 (2)	113.90 (3)	C35-C36-C37	668	122 (4)	122.33 (5)
C6-C7-C8	13	111 (2)	112.02 (3)	C35-C36-C38	668	122 (4)	120.71 (6)
C6-C7-C24	3	113 (1)	116.11 (3)	C37-C36-C38	519	114 (3)	116.90 (6)
C6-C18-C34	5	116 (2)	116.61 (3)	O1-C4-C3	94	124 (2)	121.14 (3)
C7-C6-C17	27	110 (2)	110.59 (3)	O1-C4-C5	4	120 (1)	115.56 (3)
C7-C6-C18	3	109 (1)	109.18 (3)	O2-C10-C3	8	119 (1)	119.22 (4)
C7-C24-C25	16	113 (3)	114.07 (3)	O2-C10-C11	44	113 (2)	113.92 (4)
C8-C1-C9	7	105 (2)	104.70 (3)	O3-C2-C1	7	119 (3)	118.15 (3)
C8-C1-C29	7	111 (1)	110.05 (3)	O3-C2-C3	94	124 (2)	122.15 (3)
C8-C7-C24	7	109 (2)	113.87 (3)	O4-C9-C1	31	121 (2)	122.72 (3)
C9-C1-C29	13	110 (3)	112.83 (3)	O4-C9-C5	4	122 (1)	122.07 (3)
C9-C5-C19	3	110 (1)	110.72 (3)	O5-C15-C14	432	118 (2)	120.09 (4)
C10-C11-C12	78	120 (2)	117.95 (4)	O5-C15-C16	2565	119 (3)	118.91 (4)
C10-C11-C16	10	119 (2)	123.55 (4)	O6-C14-C13	4104	119 (3)	124.54 (4)
C11-C12-C13	10000	120 (1)	121.28 (4)	O6-C14-C15	432	118 (2)	115.91 (4)