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Supporting information for article:

Peculiarities of supramolecular organization of cyclic ketones with vinylacetylene fragments

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Supporting information

2,5-Bis(3-phenylprop-2-yn-1-ylidene)cyclopentanone (3a). Yellow needles (71%), m.p. 150–151°C (acetone–H_2O). IR (KBr, cm^{-1}): 2182, 1680, 1600, 1210, 755, 687; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.52–7.55 (m, 4H, H-arom.), 7.35–7.40 (m, 6H, H-arom.), 6.81 (s, 2H, =CH), 2.97 (s, 4H, CH_2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 191.8, 149.5, 132.0, 129.4, 128.5, 122.6, 114.6, 103.0, 87.7, 25.2. MS, *m/z* (*I*, %): 308 (29) $[M]^+$, 279 (16), 202 (13), 152 (11), 139 (100), 114 (28), 89 (12), 77 (15), 63 (15). Elemental analysis calcd. for $C_{23}H_{16}O$: C, 89.58; H, 5.23. Found: C, 89.53; H, 5.17.

2,5-*Bis*(3-(4-bromophenyl)prop-2-yn-1-ylidene)cyclopentanone (3b). Yellow needles (88%), m.p. 215–216°C (1,4-dioxane–H_2O). IR (KBr, cm^{-1}): 2183, 1687, 1602, 1215, 758, 685; ^{1}H NMR (400 MHz, DMSO-d_6) δ δ 7.59 (d, 4H, *J* = 8.5Hz, H-arom.), 7.45 (d, 4H, *J* = 8.5Hz, H-arom.), 6.63 (s, 2H, =CH), 2.91 (s, 4H, CH_2); ^{13}C NMR (100 MHz, DMSO-d_6) δ 191.2, 151.0, 134.0, 132.4, 123.7, 121.8, 113.3, 101.4, 89.2, 25.6. Elemental analysis calcd. for $C_{23}H_{14}Br_2NO$: C, 59.26; H, 3.03. Found: C, 59.19; H, 3.10.

2,6-*Bis*(3-phenylprop-2-yn-1-ylidene)cyclohexanone (3c). Yellow needles (85%), m.p. 149–151°C (acetone–H_2O). IR (KBr, cm^{-1}): 2935, 2190, 1658, 1597, 1308, 1245, 3f3, 1140, 901, 756, 727, 658; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.52–7.55 (m, 4H, H-arom.), 7.34–7.39 (m, 6H, H-arom.), 7.01 (s, 2H, =CH), 2.93–2.97 (m, 4H, CH_2), 1.85–1.94 (m, 2H, CH_2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 186.3, 145.4, 131.9, 129.2, 128.5, 122.7, 118.3, 103.9, 87.5, 29.0, 21.7. MS, *m/z* (*I*, %): 322 (65) $[M]^+$, 294 (27), 278 (17), 265 (29), 252 (12), 215 (33), 202 (17), 189 (10), 178 (20), 165 (13), 152 (53), 139 (100), 115 (65), 102 (24), 89 (27), 77 (43), 63 (26), 51 (17). Elemental analysis calcd. for $C_{24}H_{18}O$: C, 89.41; H, 5.63. Found: C, 89.33; H, 5.69.

2,6-*Bis*(3-(4-bromophenyl)prop-2-yn-1-ylidene)cyclohexanone (3d). Yellow needles (89%), m.p. 150–151°C (acetone–H_2O). IR (KBr, cm^{-1}): 2187, 1655; ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.67 (d, 4H, *J* = 8.4Hz, H-arom.), 7.52 (d, 4H, *J* = 8.4Hz, H-arom.), 6.83 (s, 2H, =CH), 2.88–2.92 (m, 4H, CH_2), 1.81–1.87 (m, 2H, CH_2); ^{13}C NMR (75 MHz, DMSO-d_6) δ 186.8, 146.7, 133.6, 132.0, 123.3, 120.9, 116.4, 101.9, 88.3, 28.5, 21.1. Elemental analysis calcd. for $C_{24}H_{16}BrO_2$: C, 60.03; H, 3.36. Found: C, 60.11; H, 3.38.

4-(*tert*-Butyl)-2,6-*bis*(3-phenylprop-2-yn-1-ylidene)cyclohexanone (3e). Yellow needles (74%), m.p. 168–169°C (acetone–H_2O). IR (KBr, cm^{-1}): 2961, 2187, 1648, 1576, 1315, 1233, 1162, 929, 757, 718, 688; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.51–7.54 (m, 4H, H-arom.), 7.35–7.40 (m, 6H, H-arom.), 6.98–6.99 (m, 2H, =CH), 3.30–3.36 (m, 2H, CH_2), 2.32–2.42 (m, 2H, CH_2), 1.53–1.64 (m, 1H, CH_2), 1.08 (s, 9H, *t*-Bu); ^{13}C NMR (75 MHz, $CDCl_3$) δ 186.5, 145.7, 131.9, 129.2, 128.6, 122.8, 118.2, 103.9, 87.4, 43.2, 32.6, 30.4, 27.3. MS, *m/z* (*I*, %): 378 (53) $[M]^+$, 350 (37), 289 (25), 278 (14), 265 (20), 252 (10), 215 (19), 189

(16), 178 (10), 165 (23), 152 (30), 139 (100), 115 (48), 102 (10), 91 (12), 77 (15), 57 (87), 55 (22). Elemental analysis calcd. for $C_{28}H_{26}O$: C, 88.85; H, 6.92. Found: C, 88.77; H, 6.89.

4-(*tert*-Butyl)-2,6-*bis*(3-(4-methylphenyl)prop-2-yn-1-ylidene)cyclohexanone (3f). Yellow needles (72%), m.p. 128–130°C (acetone–H_2O). IR (KBr, cm^{-1}): 2183, 1656; ^1H NMR (300 MHz, $CDCl_3$) δ 7.42 (d, 4H, *J* = 8.0 Hz, H-arom.), 7.19 (d, 4H, *J* = 8.0Hz, H-arom.), 6.97–6.98 (m, 2H, =CH), 3.30–3.34 (m, 2H, CH_2), 2.32–2.40 (m, 8H, CH_2 + CH_3), 1.54–1.62 (m, 1H, CH_2), 1.08 (s, 9H, *t*-Bu); ^{13}C NMR (75 MHz, $CDCl_3$) δ 186.5, 145.3, 139.6, 131.8, 129.3, 119.8, 118.3, 104.3, 87.1, 43.3, 32.6, 30.4, 27.2, 21.6. Elemental analysis calcd. for $C_{30}H_{30}O$: C, 88.63; H, 7.44. Found: C, 88.57; H, 7.51.

Synthesis of compound 4

Aqueous solution of sodium hydroxide (1%, 330 mL) was added to a mixture of cyclohexanone (54.8 g, 0.56 mol) and freshly distilled furfural (26.7 g, 0.28 mol) being vigorous stirring. The reaction mixture was stirred for 4 hours, then dilute HCl was added (to pH 5). The precipitated oil was separated and the aqueous layer was extracted three times with benzene. The benzene extract and oil were dried with Na_2SO_4, and the solvent was distilled off in vacuo. The residue was distilled in vacuo (20.7 g, 42%), yellowish liquid (crystallizes): b.p. 177–179°C (18 mm Hg); m.p. 49–50°C (from petroleum ether). ^1H NMR (300 MHz, $CDCl_3$) δ 7.46 (s, 1H, =CH), 7.29–7.31 (m, 1H, H-furan), 6.53 (d, *J* = 3.30 Hz, 1H, H-furan), 6.40–6.42 (m, 1H, H-furan), 2.78–2.82 (m, 2H, CH_2), 2.38–2.42 (m, 2H, CH_2), 1.68–1.84 (m, 4H, CH_2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 199.8, 152.1, 144.3, 132.2, 122.7, 115.8, 112.1, 39.6, 28.2, 22.9, 22.7.

2-(Furan-2-ylmethylene)-6-(3-phenylprop-2-yn-1-ylidene)cyclohexanone (5a). Yellow needles (83%), m.p. 105–106°C (C_6H_6–C_6H_{14}). IR (KBr, cm^{-1}): 2933, 3015, 1650, 1598, 1586, 1553, 1303, 1245, 1168, 1017, 960, 760; ^1H NMR (300 MHz, $CDCl_3$) δ 7.50–7.60 (m, 4H, H-arom.+ =CH), 7.35–7.37 (m, 3H, H-arom. + H-furan.), 6.98 (s, 1H, =CH), 6.69 (d, *J* = 3.30 Hz, 1H, H-furan.), 6.52–6.54 (s, 1H, H-furan.), 2.90–3.02 (m, 4H, CH_2), 1.84–1.92 (m, 2H, CH_2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 187.4, 152.6, 145.9, 144.8, 132.3, 131.8, 129.0, 128.4, 124.2, 122.8, 3f.1, 116.7, 112.4, 103.0, 87.5, 28.8, 28.2, 21.6. Elemental analysis calcd. for $C_{20}H_{16}O_2$: C, 83.31; H, 5.59. Found: C, 83.41; H, 5.63.

2-(Furan-2-ylmethylene)-6-(hept-2-yn-1-ylidene)cyclohexanone (5b). Yellow needles (75%), m.p. 38–39°C (C_6H_6–C_6H_{14}). IR (KBr, cm^{-1}): 2958, 2935, 2868, 2205, 1653, 1595, 1567, 1554, 1305, 1280, 1164, 1142, 1037, 771, 738; ^1H NMR (300 MHz, $CDCl_3$) δ 7.52–7.53 (m, 2H, furan.+ =CH), 6.72 (s, 1H, =CH), 6.64 (d, 1H, *J* = 3.30 Hz, H-furan.), 6.49 (s, 1H, H-furan.), 2.92–2.96 (m, 2H), 2.74–2.78 (m, 2H, CH_2), 2.41–2.45 (m, 2H, CH_2), 1.74–1.84 (m, 2H, CH_2), 1.40–1.60 (m, 4H, CH_2), 0.90–0.94 (m, 3H, Me); ^{13}C NMR (75 MHz, $CDCl_3$) δ 187.6, 152.6, 144.6, 144.9, 132.3, 123.8, 118.2, 116.3, 112.3, 105.5, 78.7, 30.6, 28.2, 21.9, 19.7, 13.5. MS, *m/z* (*I*, %): 268 (100) $[M]^+$, 253 (4) $[M–Me]^+$, 239 (37) $[M–Et]^+$, 225 (21) [*M*–

Pr]$^+$, 197 (16), 183 (10), 155 (15), 141 (20), 128 (13), 115 (13), 91 (17), 77 (11). Elemental analysis calcd. for $C_{18}H_{20}O_2$: C, 80.56; H, 7.51. Found: C, 80.47; H, 7.58.