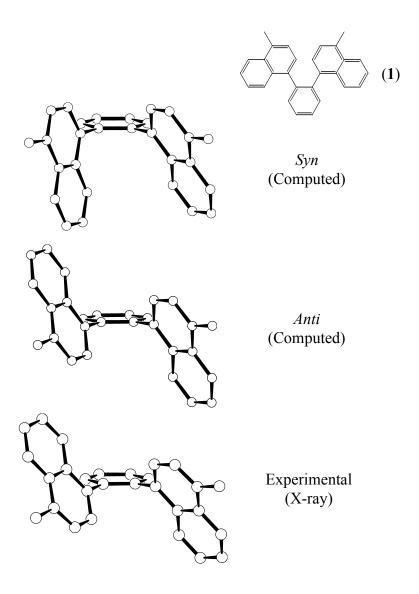
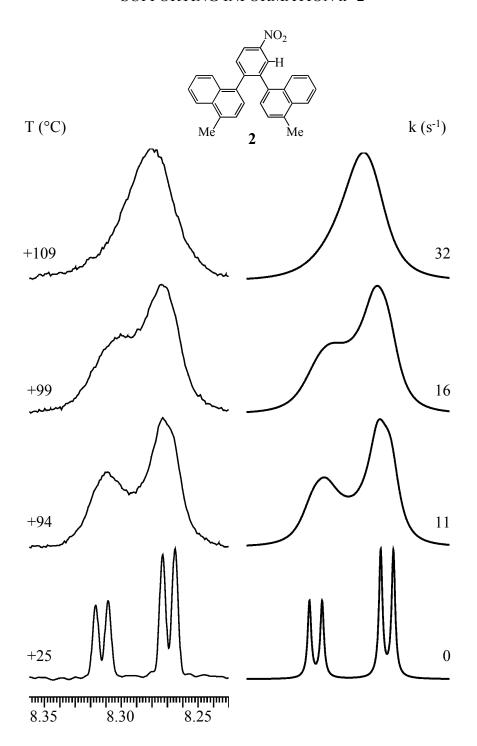
SUPPORTING INFORMATION n° 1



<u>Top</u>: MMX computed structures of the *anti* and *syn* conformational diastereoisomers of 1. <u>Bottom</u>: single diastereoisomer observed by X-ray diffraction.

SUPPORTING INFORMATION n° 2



<u>Left</u>: experimental ¹H NMR (300 MHz) signals of the hydrogen in position 3 of the phenyl ring of compound **2** in toluene-d8 as function of temperature. <u>Right</u>: computer simulation obtained with the rate constants reported.

SUPPORTING INFORMATION n° 3

Synthesis of 1,2-bis(1-naphthyl)-4-nitrobenzene (3) from 3,4-dinitrothiophene

Compound **3** was prepared through a proper adaptation of a reported procedure* starting from 1,4-bis(diethylamino)-2,3-dinitro-1,3-butadiene, easily obtainable via a ring-opening reaction of 3,4-dinitrothiophene with diethylamine.[#]

1,2-Bis(1-naphthyl)-4-nitrobenzene (3). A solution of (*E,E,E*)-1,6-bis(1-naphthyl)-3-nitro-1,3,5-hexatriene (0.4 mmol), iodine (2 mmol) and cyclohexene oxide (0.8 mmol) in toluene (500 mL) was heated overnight at 80 °C. Usual workup* and purification by column chromatography gave 0.37 mmol (92%) of **3** with physical and spectroscopic data in agreement with those reported in the Experimental Section.

(*E,E,E*)-1,6-Bis(1-naphthyl)-3-nitro-1,3,5-hexatriene. 1,4-Bis(diethylamino)-2,3-dinitro-1,3-butadiene (1 mmol) in THF (30 mL) was reacted, under argon and at 0 °C, with (1-naphthyl)methylmagnesium bromide (4 mmol) freshly prepared in THF/xylene (5:1, v/v). After 30 min, the reaction mixture was poured into a dichloromethane/ice/HCl (4 mmol) mixture and worked up as reported.* The title hexatriene was obtained in 81% yield as a red solid, m.p. 104.7-105.3°C (dichloromethane-light petroleum); 1 H-NMR (CDCl₃, 200 MHz) δ 7.20 and 7.29 (d, J = 16.2 Hz, 2H in total), 7.53 (m, 7H), 7.87 and 8.11 (two m partly overlapped, 10 H in total); 13 C-NMR (CDCl₃, 50 MHz) δ 119.14, 123.07, 123.45, 124.39, 124.46, 124.86, 125.62, 125.74, 126.26, 126.44, 126.80, 127.14, 128.90, 129.02, 129.63, 130.61, 131.29, 132.89, 133.66, 133.80, 133.91, 134.15, 135.02, 137.88, 141.52, 148.03. Anal. Calcd for C₂₆H₁₉NO₂: C, 82.74; H, 5.07; N, 3.71. Found: C, 82.83; H, 5.15; N, 3.66.

^{*} Dell'Erba, C; Gabellini, A.; Mugnoli, A.; Novi, M.; Petrillo, G.; Tavani, C. *Tetrahedron* **2001**, 9025.

[#] Dell'Erba, C.; Mele, A.; Novi, M.; Petrillo, G.; Stagnaro, P. *Tetrahedron Lett.* **1990**, *31*, 4933. Dell'Erba, C.; Mele, A.; Novi, M.; Petrillo, G.; Stagnaro, P. *Tetrahedron* **1992**, *48*, 4407.