Supporting information for

Twist-dependent Electronic Coupling in an Organic Intervalence Radical Cation

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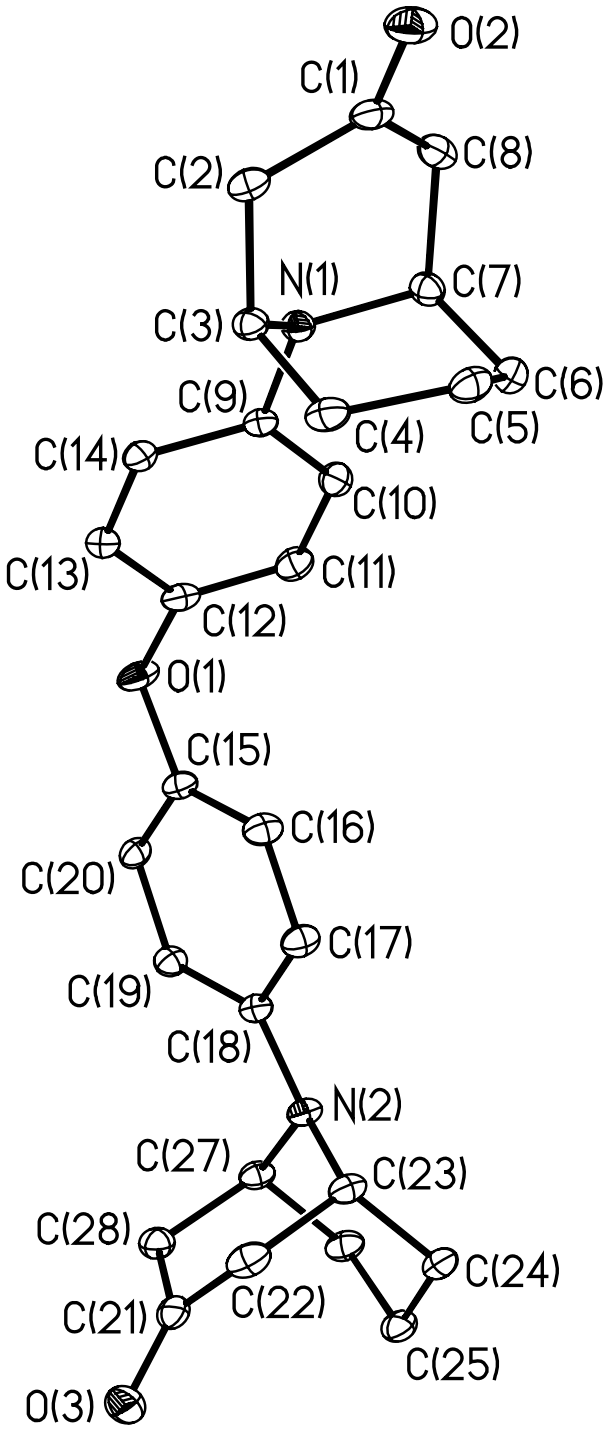
Bis[4-(3'-keto-9'-azabicyclo[3.3.21]non-9'-yl)phenyl] ether (3) A mixture of 1.23 g (6.14 mmol) of 4,4'-diaminodiphenylether and 1.50 g (12.28 mmol) of 2.7-cycloocta-dieneone[S1] in 6 mL of methanol was stirred at room temperature for a week. After filtration the crude product was purified by chromatography using 30% (v/v) ethl acetate in hexane as solvent, giving 0.98 g (36%) of **3**, m.p. 189-191^{o}C. ^{1}H-NMR: δ 6.97-6.90 (m, 8H), 4.40 (br s, 4H), 2.68 (dd, J = 16.4, 6.6 Hz, 4H), 2.39 (d, J = 16.3 Hz, 4H), 2.0-1.93 (m, 4H), 1.79-1.62,(m, 8H). ^{13}C-NMR δ 209.97, 150.08, 143.77, 119.76, 115.27, 51.46, 43.56, 30.39, 16.54. IR (KBr) cm^{-1} 1702, 1600, 1500, 1099. The x-ray structure appears below.

9-(4'-phenoxyphenyl)-9-azabicyclo[3.3.1]non-3-one (4) A mixture of 0.294 g (1.59 mmol) of 4-dimetylaminodiphenyl ether and 0.194 g (1.59 mmol) of 2.7-cycloocta-dieneone[S1] was stirred in 15 mL methanol for a week. After filtration the product was purified by washing with cold methanol and drying under vacuum, giving 0.30 g of **4**, m.p. 121-122^{o}C. ^{1}H-NMR: δ 7.32-6.93 (m, 2H), 7.06-6.93 (m, 7H), 4.41 (br s, 2H), 2.73-2.65 (dd, J = 16.5, 6.5 Hz, 2H), 2.43-2.37 (d, J = 16.3 Hz, 2H), 2.04-1.93 (m, 2H), 1.78-1.73,(m, 2H), 1.69-1.62(m, 4H). ^{13}C-NMR δ 209.87, 158.55, 148.52, 144.46, 129.53, 122.29, 121.14, 117.46, 115.33, 51.44, 43.65, 30.40, 16.56.

Radical cation formation: A mixture of 10.0 mg **3** and 2.5 mg $NO^{+}BF_4^{-}$ (0.95 eq.) in a flame-dried test tube, under nitrogen, containing a stirring bar was treated under nitrogen with 3 mL of deaerated methylene chloride which had been freshly distilled from calcium hydride. The solution becomes brick-red immediately, and.may be stored at -22^{o}C for days without loss of the red color, but fades rapidly at room temperature even when the tube is stoppered with a rubber septum. No resolution was achieved in the ESR spectrum of $\mathbf{3}^{+}$. The solution of $\mathbf{4}^{+}$ used for the optical spectrum was prepared in the same way.

(S1) (a) Garbisch, E. W. Jr. *J. Org. Chem.* **1965**, *30*, 2109. (b) Krabbenhoft, H. O. *J. Org. Chem.* **1979**, *44*, 4285.


O(2)
C(1)
C(8)
C(2)
N(1)
C(7)
C(3)
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