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Supporting Information

Photophysical properties of benzanthrone derivatives: Effect of substituent, solvent polarity and hydrogen bonding

Shivraj¹, B. Siddlingeshwar^{1*}, Elena M.Kirilova², SergeyV.Belyakov³, Darshan Devang Divakar⁴, Abdulaziz Abdullah Alkheraif⁴

¹Department of Physics, M.S. Ramaiah Institute of Technology, Bengaluru-560054, India

²Department of Chemistry, Daugavpils University, Vienibas 13, Daugavpils, Latvia

³Latvian Institute of Organic Synthesis, Aizkraukles str. 21, Riga LV-1006, Latvia

⁴ Dental Biomaterials Research Chair, Dental Health Department, College of Applied Medical Sciences, King Saud University, Riyadh 11433, KSA

*Correspondence to: B. Siddlingeshwar, E-mail: sidduphysics@gmail.com

Synthesis:

Benzanthrone derivatives ([Me-PBA] and, [Ph-PBA]) were synthesized according to the procedure reported in the literature^{7, 8}.

IR spectra were recorded on the SHIMADZU Prestige-21FT spectrometer in KBr pellets.

¹H and ¹³C NMR spectra were recorded on the Bruker AVANCE 300 spectrometer operating at 300 MHz in CDCl₃ (with TMS as an internal standard) at an ambient temperature. The chromatomass spectroscopic studies were carried out using the Shimadzu QP2010 chromatograph with EI ionization, 70 eV, the mass range 39–400 m/z.

3-N-[N'-methylpiperazino]benzanthrone was obtained from 3-bromobenzanthrone with yield 50% as orange powder with m.p.184 °C.

IR v_{max} (KBr), cm⁻¹: 1576 (C=C); 1642 (C=O); 2812, 2936, 3072 (C-H)

¹H NMR δ, ppm. (CDCl₃): 2.39 (3H, s, CH3); 2.70 (4H, m, CH2); 3.20 (4H, m, NCH2); 7.48-8.73 (9H, m, CH arom.).

¹³C NMR δ, (CDCl₃): 53.8, 56.2, 117.2, 121.8, 122.3, 123.3, 125.7, 126.1, 126.6, 127.9, 129.0, 129.6, 132.0, 133.5, 134.2, 143.8, 183.9.

MS (*m*/*z*): 328 [M+] (50), 281 (30), 257 (16), 243 (29), 228 (12), 207 (53), 202 (12), 200 (12), 72 (22), 70 (24).

3-N-[N'-phenylpiperazino]benzanthrone was obtained from 3-bromobenzanthrone with yield 58% as orange needles crystals with m.p. 252°C.

IR v_{max} (KBr), cm⁻¹: 1576, 1597 (C=C); 1645 (C=O); 2342, 2361, 3436 (C-H).

¹H NMR δ, ppm. (CDCl₃): 3.41 (s, 4H, NCH₂); 3.58 (s, 4H, NCH₂); 6.96 (t, 1H, J=7.3 Hz, C5-H); 7.07 (d, 1H, J=8 Hz, C2-H); 7.36-7.56 (m, 5H, Ph); 7.75 (dt, 1H, J=7.8; 1.6 Hz, C9-H); 7.82 (dt, 1H, , J=7.8; 1.3 Hz, C10-H); 8.31 (d, 1H, J=8 Hz, C1-H); 8.43 (d, 1H, J=8.2 Hz, C4-H); 8.52 (dd, 1H, J=7.8; 1.3 Hz, C11-H); 8.67 (dd, 1H, J=8.2; 1.3 Hz, C8-H); 8.83 (dd, 1H, J=7.3; 1.3 Hz, C6-H).

¹³C NMR δ, (CDCl₃): 49.7, 53.5, 115.2, 116.3, 120.2, 122.2, 122.7, 125.0, 125.9, 127.5, 128.1, 128.2, 129.3, 129.9, 130.4, 130.8, 133.3, 136.5, 152.3, 184.6.

MS (*m/z*): 390 [M+] (96), 375 (10) 284 (12), 257 (24), 243 (38), 228 (20), 201 (17), 132 (40), 105(45), 77 (18).

Crystal structure analysis

Diffraction data were collected at low temperature ($T = -90^{\circ}$ C) on a Bruker-Nonius Kappa CCD diffractometer using graphite monochromated Mo-K α radiation ($\lambda = 0.71073$ Å). The crystal structure was solved by direct methods and refined by full-matrix least squares procedure using programs. For further details, see crystallographic data for the compounds deposited at the Cambridge Crystallographic Data Centre as Supplementary Publication Number CCDC 1538700. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK.

The structure of Ph-PBA was determined by X-ray structure analysis. Figure S1 illustrates the ORTEP diagram of the molecular structure of this compound. In crystals the molecular plane obtained by the least square method almost corresponds to the crystallographic plane (2 $\overline{2}$ 1). This plane practically coincides with the benzanthrone ring. The piperazine cycle is characterized by the chair conformation; its least-square plane turns about C3–N18 bond on 49.1(3)° concerning the benzanthrone ring. Dihedral angle between the phenyl ring and the piperazine least-square plane is equal 28.2°.



Figure S1. Molecular structure of Ph-PBA with labels of atoms and thermal ellipsoids.



Figure S2: Time-resolved emission traces for Me-PBA in few representative solvents measured by TCSPC technique.



Figure S3: Emission decay traces of Ph-PBA in different solvents measured by fluorescence upconversion technique. Solid lines are the fit to the experimental data. The lifetimes obtained from the exponential fit are given in the Table 1 in the main text of the article.



Figure S4: Time-resolved emission decay traces of (A) Me-PBA measured by TCSPC technique and (B) Ph-PBA measured by fluorescence up-conversion technique in methanol-glycerols mixtures.