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The synthesis, spectroscopic characterization and structure of three bis(arylmethylidene)cyclopentanones

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ABSTRACT

Three bis(arylmethylidene)cyclopentanone dyes were synthesized and their structures and properties elucidated using single-crystal X-ray diffraction, mass spectrometry, ^{1}H nuclear magnetic resonance, IR and UV–Vis spectroscopy. X-ray analyses revealed that two were monoclinic, with space group $P2_1/c$, while the third dye was triclinic, with space group $P\bar{1}$. All three molecules adopted an *E*-configuration about the central olefinic bonds, exhibiting a butterfly-shaped geometry. Molecular structure optimization using density function theory revealed that the optimized geometer parameters were in reasonably good agreement with experimental values. In addition, the highest occupied molecular orbital and lowest unoccupied molecular orbital levels were deduced.

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1. Introduction

The bis(arylmethylidene)cycloalkanone moiety is both a novel pharmacophore and an important chromophore. Molecules that comprise such a structural unit are of special interest owing to their broad spectrum of activities and applications. Curcumin (Fig. 1) is a naturally occurring yellow pigment isolated from the root of *Curcuma longa* rhizomes, and exhibits a wide range of biological activities [1–5]. As a class of conjugated monoketone analogues of Curcumin, the bis(arylmethylidene)cycloalkanones have been already reported to posses potential anti-HIV protease activity, cytotoxic, cancer chemopreventive and antioxidant properties [6–14]. Furthermore, these compounds are more compact than Curcumin and are readily synthesized. Recent, it has been reported that some compounds containing the 3-(3,4,5-trimethoxyphenyl)-2-propenoyl group displayed potent multidrug resistance (MDR) reversal properties in cancer chemotherapy. In particular, 2,5-bis(3,4,5-trimethoxyphenylmethylene) cyclopentanone (**TMPCP**) (Fig. 1) was 31 times more potent than Verapamil as a MDR revertant [15].

On the other hand, some bis(arylmethylidene)cycloalkanones are found be effective photosensitive materials and fluorescent probe, and exhibit promising two-photon absorption (TPA) properties [16–19]. For example, bis(benzylidene)cyclopentanone derivatives **MPCP** and **EPCP** (Fig. 1) are well-known high-efficient sensitizing dye that is widely employed in photopolymerization systems. Also, in a very recent study it was shown that these two bis(benzylidene)cyclopentanone dyes displayed large two-photon absorption cross-sections [20,21]. Besides, bis(arylmethylidene) cycloalkanones are widely used as building blocks for the synthesis of a new class of spiro pyrrolidines as antimicrobial and antifungal agents, tricyclic thiazolo[3,2-*a*] thiapyrano[4,3-*d*] pyrimidines and related analogues as potential anti-inflammatory agents and other bioactive heterocycles [6,22,23].

As a part of our continuous interest in the synthesis, crystallography and optical evaluation of bis(arylmethylidene)cycloalkanone derivatives, three bis(arylmethylidene) cyclopentanone dyes, **1**, **2** and **3** (Fig. 2), were synthesized. Herein, we report the synthesis, crystal structure and spectroscopic characterization of these three dyes. At the same time, the molecular structures of **1** and **3** were optimized using density function theory (DFT) at B3LYP/6-31G level.

2. Experimental

2.1. Chemicals and instrument

All melting points were determined with a WRS-1A melting point apparatus and are uncorrected. Proton nuclear magnetic

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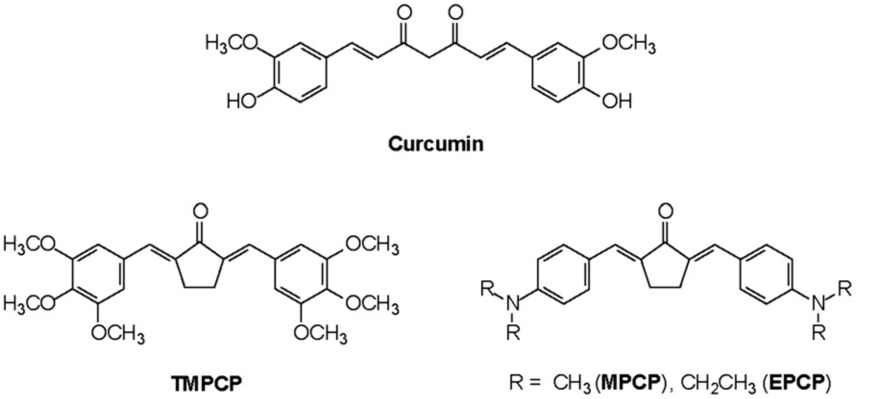

Fig. 1. The structures of Curcumin, TMPCP, MPCP and EPCP.

resonance (^{1}H NMR) spectra were run on a Bruker AV-400 or DRX-500 NMR spectrometer and chemical shifts expressed as δ (ppm) values with TMS as internal standard. IR spectra were recorded in KBr on a Nicolet NEXUS 870 FT-IR spectrophotometer. Vibrational transition frequencies are reported in wave numbers (cm^{-1}). The UV spectra were recorded using a Helios Alpha UV–Vis scanning spectrophotometer. Element analysis was taken with a Perkin–Elmer 240 analyzer. Mass spectra (MS) were measured on a LCQ Advantage MAX or VG ZAB-HS mass spectrometer. Single crystal was characterized by Enraf-Nonius CAD-4 or Bruker Smart 1000 CCD X-ray single-crystal diffractometer. All the chemicals are commercially available and they were used without further purification.

2.2. Synthesis

*2.2.1. 2,5-Bis-(3-phenoxybenzylidene)cyclopentanone (**1**)*

For the preparation of the title compound, 5 mmol of cyclopentanone and 10 mmol of 3-phenoxybenzaldehyde were dissolved in 20 mL of ethanol. To this solution, an aqueous solution (15 mL) of sodium hydroxide (75 mmol) was added dropwise with stirring at room temperature. The reaction mixture was stirred for a further 3 h and then poured into a mixture of ice and concentrated hydrochloric acid. The precipitate was filtered by suction and washed thoroughly with water and finally with ethanol. The product was dried at room temperature and crystallized from ethanol to give **1** as yellow crystals, yield 67%, mp 155–157 °C; ^{1}H NMR (400 MHz, $CDCl_3$/TMS) δ: 3.04 (s, 4H, $2 \times CH_2$), 7.03–7.08 (m, 6H, Ar-H), 7.17 (t, $J = 7.3$ Hz, 2H, Ar-H), 7.24 (t, $J = 1.8$ Hz, 2H, Ar-H), 7.32–7.44 (m, 8H, Ar-H), 7.55 (s, 2H, $2 \times {=}CH{-}$). IR (KBr) ν: 1685, 1629, 1593, 1568, 1496, 1455, 1434, 1230, 1199, 1158, 1071, 948, 892, 753, 671 cm^{-1}. MS m/z: 445 (M + 1). Anal. calcd for $C_{31}H_{24}O_3$: C 83.76, H 5.44; found: C 83.52, H 5.75.

*2.2.2. 2,5-Bis-(3,5-di-tert-butyl-4-hydroxybenzylidene) cyclopentanone (**2**)*

The title compound was prepared by the acid catalyzed reaction of 3,5-di-tert-butyl-4-hydroxybenzaldehyde with cyclopentanone, as previously described in [24,25] with modification. 20 mmol of 3,5-di-tert-butyl-4-hydroxybenzaldehyde and 10 mmol of cyclopentanone were dissolved in 30 mL of methanol. To this solution, 1.5 mL concentrated sulfuric acid was added dropwise with stirring at room temperature, which continued for 0.5 h. Then, the reaction mixture was refluxed for 3 h. After cooling, the mixture was treated with cold water and filtered. The solid obtained was then washed and dried. The crude product was recrystallized from ethanol to give **2** as yellow crystals, yield 49%; ^{1}H NMR (400 MHz, DMSO-d_6/TMS) δ: 1.42 (s, 36H, $12 \times CH_3$), 3.05 (s, 4H, $2 \times CH_2$), 7.37 (s, 2H, OH), 7.44 (s, 4H, Ar-H), 7.52 (s, 2H, $2 \times {=}CH{-}$). IR (KBr) ν: 3611, 3406, 1665, 1619, 1588, 1424, 1322, 1255, 1184, 1127, 1009, 943, 876, 774, 605, 492 cm^{-1}. MS m/z: 517 (M + 1). Anal. calcd for $C_{35}H_{48}O_3$: C 81.35, H 9.36; found: C 81.12, H 9.23.

*2.2.3. 2,5-Bis-(9-anthrylmethylidene)cyclopentanone (**3**)*

This compound was prepared according to the procedure described for **1**, from 20 mmol 9-anthrylaldehyde and 10 mmol cyclopentanone. Red crystals, yield 56%, mp > 235 °C; ^{1}H NMR (500 MHz, $CDCl_3$/TMS) δ: 2.30 (s, 4H, $2 \times CH_2$), 7.48–7.54 (m, 8H, Ar-H), 8.01–8.12 (m, 8H, Ar-H), 8.47 (s, 2H, Ar-H), 8.59 (s, 2H, $2 \times {=}CH{-}$). IR (KBr) ν: 1676, 1634, 1627, 1441, 1408, 1359, 1310, 1207, 1157, 1089, 956, 890, 847, 796, 735, 728, 535, 512 cm^{-1}. MS m/z: 461.00 (M + 1). Anal. calcd for $C_{35}H_{24}O$: C 91.27, H 5.25; found: C 91.53, H 5.18.

2.3. X-ray crystallography

Suitable single crystals of **1**, **2** and **3** for X-ray structural analysis were obtained by evaporation of ethanol or DMF

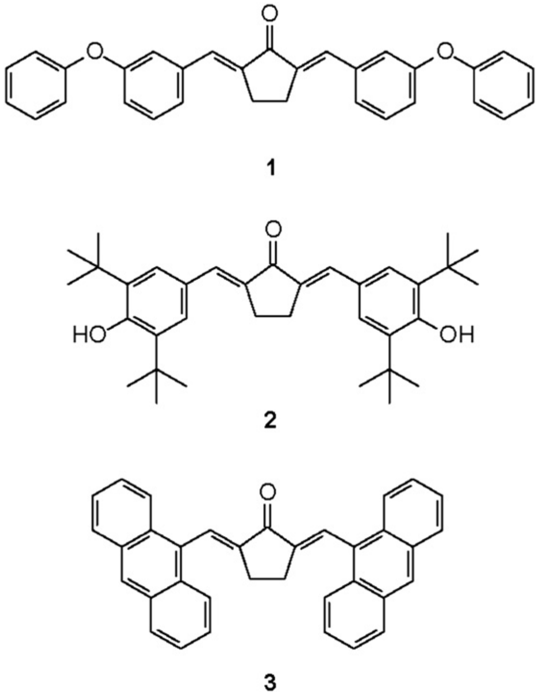

Fig. 2. The structures of bis(arylmethylidene)cyclopentanones.

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