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Structural characterizations, Hirshfeld surface analyses, and third-order nonlinear optical properties of two novel chalcone derivatives

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ABSTRACT

We report synthesis, characterizations, structure-property relationships, and third-order nonlinear optical studies for two new chalcone derivatives, (2*E*)-1-(anthracen-9-yl)-3-(4-bromophenyl)prop-2-en-1-one (**Br-ANC**) and (2*E*)-1-(anthracen-9-yl)-3-(4-chlorophenyl)prop-2-en-1-one (**Cl-ANC**). These derivatives were crystallized in the centrosymmetric monoclinic $P2_1/c$ crystal structure. The intermolecular interactions of both the crystals were visualized by Hirshfeld surface analyses (HSA). The crystals are thermally stable up to their melting points (180.82 and 191.16 °C for **Cl-ANC** and **Br-ANC**, respectively). The geometry optimizations, FT-IR spectra, ^{1}H and ^{13}C NMR spectra, electronic absorption spectra, electronic transitions, and HOMO-LUMO energy gaps were studied by Density Functional Theory (DFT) at B3LYP/6-311+G(d, p) level. The theoretical results provide excellent agreement with experimental findings. The electric dipole moments, static polarizabilities, molecular electrostatic potentials (MEP) and global chemical reactivity descriptors (GCRD) were also theoretically computed. The materials exhibited good nonlinear absorption (NLA), nonlinear refraction (NLR) and optical limiting (OL) behavior under diode-pumped solid-state (DPSS) continuous wave (CW) laser excitation (532 nm and 200 mW). The NLO parameters such as NLA coefficient (β~10^{-5} cmW^{-1}), NLR index (n_2~10^{-10} cm^2 W^{-1}) and third-order NLO susceptibilities ($\chi^{(3)}$ ~10^{-7} esu) were measured. Further, we estimated one-photon and two-photon figures of merit, which satisfy the demands ($W > 1$ and $T < 1$) for all-optical switching. Thus, the present chalcone derivatives with anthracene moiety are potential materials for OL and optical switching applications.

1. Introduction

The nonlinear optics is a very interesting field for physicists and engineers to fabricate new devices for various applications in the areas such as telecommunications, photonics, sensors, harmonic generations, detection of explosives, protection of photosensitive instruments etc. [1–4]. The material preparation and crystal design for these applications are great challenges for researchers [5,6]. Moreover, the structural and nonlinear optical characterizations of several types of materials such as thin films, nano composites, organic and inorganic crystals have become an extremely important in understanding their structure-property relationships for various applications in nonlinear optics [7–10]. Although there are currently many available nonlinear optical (NLO) materials, researchers are still looking for the easy-synthesizable materials with higher-order of optical nonlinearity and lower cost.

The chalcone derivatives have attracted significant attention in the past few decades mainly because of their availability in natural products [11], structural flexibility, biological activities [12,13], and high optical nonlinearities that they can exhibit due to the significant delocalization of the electronic clouds [14,15]. One could expect high NLO activity from the donor-acceptor substituted chalcone derivatives due to their push-pull configurations [16,17]. Further, the high crystallinity of chalcones is advantageous for second and third-order NLO applications [18–20]. There are various reports about the NLO properties of chalcones performed by the pulsed wave lasers [21,22], but very few studies were carried out utilizing continuous wave laser [23]. Recently, many

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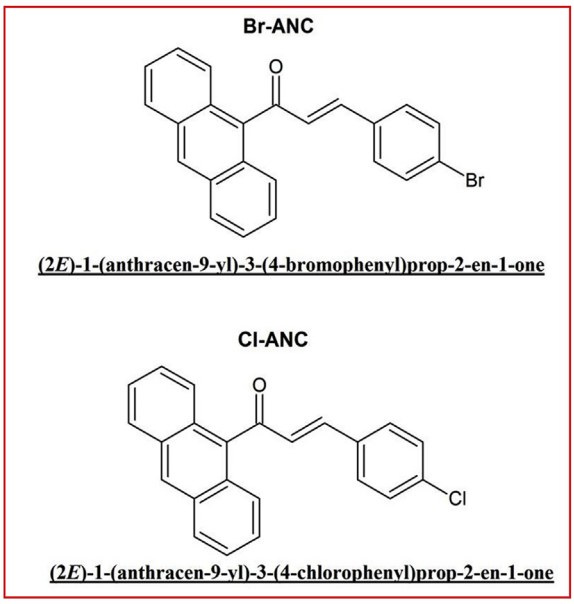

Fig. 1. The chemical structures of the synthesized chalcone derivatives.

researchers have devoted their interests in the combined experimental and theoretical studies [24–27]. The theoretical predictions would help one to understand the molecular properties without even synthesizing them, whereas the experimental findings would apparently prove the practicality and real-time applications of that material.

The main aim of this study was to synthesize new derivatives of chalcone for NLO applications and to determine the correlation between the chemical structures with their optical nonlinearity. Following this idea, we have prepared two asymmetric chalcone derivatives: (2*E*)-1-(anthracen-9-yl)-3-(4-chlorophenyl)prop-2-en-1-one (**Cl-ANC**) and (2*E*)-1-(anthracen-9-yl)-3-(4-bromophenyl)prop-2-en-1-one (**Br-ANC**) containing chloro and bromo as electron donating group, and reported their spectral characterizations, crystallographic structures, Hirshfeld surface analyses, third-order NLO measurements and DFT studies. The combined experimental and theoretical investigations such as Fourier transform infrared (FT-IR), nuclear magnetic resonance (NMR) spectroscopies, UV–Vis absorption spectra, energy band gaps, electrostatic potentials, electric dipole moments and static polarizability studies were also reported.

2. Experimental

2.1. Synthesis and crystal growth

The chalcone derivatives, **Br-ANC** and **Cl-ANC** were synthesized by the Claisen-Schmidt condensation reaction [28]. 9-acetylanthracene (0.01M) was dissolved separately with 4-bromobenzaldehyde (0.01M) and 4-chlorobenzaldehyde (0.01M) in the ethanol and a catalytic amount of NaOH was added under constant stirring for a few hours. The solution was then poured into ice-cold water and precipitate was formed. The resulting crudes were washed, filtrated, dried and purified repeatedly to get the final products of **Br-ANC** and **Cl-ANC** (Fig. 1). The obtained dried products of **Br-ANC** and **Cl-ANC** were dissolved in a mixed solvent of acetone and DMF (1:1), and heated to get rid of the contained moisture. The solution was again filtered through the Whatman filter paper and kept aside for slow evaporation for a period of 4–5 days at room temperature. The good diffraction-quality single-crystals obtained by recrystallization (Fig. 2).

2.2. Characterizations

The crystal structures of **Br-ANC** and **Cl-ANC** were determined by single-crystal X-ray diffraction method at room temperature. The X-ray data were collected by using the Bruker APEX II DUO CCD area-detector diffractometer with graphite monochromated MoK_α radiation (0.71073 Å) at a sample-to-detector distance of 5 cm. The

Table 1
Crystal data and refinement parameters of **Cl-ANC** and **Br-ANC**.

	Cl-ANC	**Br-ANC**
CCDC deposition number	1498310	1498315
Molecular formula	$C_{23}H_{15}ClO$	$C_{23}H_{15}BrO$
Molecular weight	342.80	387.26
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
a (Å)	14.5823 (13)	14.6798 (14)
b (Å)	11.0925 (10)	11.1291 (8)
c (Å)	11.4378 (10)	11.4779 (9)
α (°)	90	90
β (°)	112.8767 (15)	112.6148 (13)
γ (°)	90	90
V (Å^3)	1704.6 (3)	1731.0 (2)
Z	4	4
D_{calc} (g cm^{-3})	1.336	1.486
Crystal dimensions (mm)	0.42 × 0.26 × 0.20	0.45 × 0.38 × 0.20
Crystal color, shape	Orange, block	Orange, block
μ (mm^{-1})	0.23	2.38
Radiation, λ (Å)	Mo $K\alpha$, 0.71073	Mo $K\alpha$, 0.71073
T_{min}, T_{max}	0.839, 0.889	0.199, 0.276
Measured reflections	12427	26658
hkl range	$-19 \le h \le 16$ $-14 \le k \le 13$ $-14 \le l \le 15$	$-19 \le h \le 19$ $-14 \le k \le 14$ $-15 \le l \le 15$
θ limit (°)	2.4–28.1	1.5–28.0
Unique reflections	4127	4184
Observed reflections I > 2σ(I)	2778	3072
Parameters	226	226
Goodness of fit on F^2	1.03	1.02
R [$F^2 > 2\sigma(F^2)$], $wR(F^2)$	0.043, 0.125	0.035, 0.093

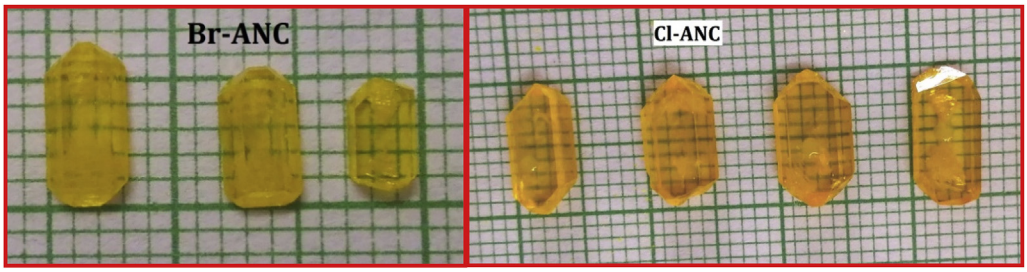

Fig. 2. The photographs of grown single-crystals of **Br-ANC** and **Cl-ANC**.