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ORIGINAL ARTICLE

Novel *N*-substituted-5-phenyl-1*H*-pyrazole-4-ethyl carboxylates as potential NLO materials

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Abstract In the present investigation we have synthesized a novel series of *N*-substituted-5-phenyl-1*H*-pyrazole-4-ethyl carboxylates, which are characterized by ^{1}H NMR, UV–Vis and FT-IR spectroscopy methods. The optical nonlinearity of the compounds in chloroform solution has been studied at 532 nm using 5 ns laser pulses, employing the open-aperture *z*-scan technique. It is found that compound **3c** having carboxylic acid group and ester substituent has maximum nonlinearity. From measurements we conclude that compounds **3c** (4-[4-(ethoxycarbonyl)-5-phenyl-1*H*-pyrazol-1-yl]benzoic acid) and **3e** (ethyl 1-(2-bromophenyl)-5-phenyl-1*H*-pyrazole-4-carboxylate) are potential candidates for optical limiting applications.

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1. Introduction

A variety of organic molecules and materials possessing large second-order nonlinearity are sought for potential applications in optical communication, information storage, optical switching, etc. (Unver et al., 2005; Williams, 1984) due to advantages such as low dielectric constants, low switching times and easy processability. The design strategy, used by many with success involves connecting donor (D) and acceptor (A) groups at the terminal positions of a p-bridge to create highly polarized molecules that could exhibit large molecular nonlinearity (Ruanwas et al., 2010). To date, the types of p-bridges investigated for developing efficient NLO materials and molecules include D–A olefines (Marder et al., 1994; Blanchard et al., 1995), acetylenes (Cheng

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et al., 1991a), azo bridges (Moylan et al., 1993), aromatic (Cheng et al., 1991b) and heteroaromatic rings (Rao et al., 1993, 1994). Although, push–pull polyenes generally show very large first hyperpolarizability β, their thermal stability is not satisfactory. On the other hand, organic molecules containing D–A systems are more stable but they exhibit relatively lower β values. Incorporation of benzene rings into the aliphatic push–pull polyenes is found to saturate molecular nonlinearity. To overcome this problem, several groups (Rao et al., 1993, 1994; Dirk et al., 1990, 1992) have developed NLO chromophores containing easily polarizable five membered heteroaromatic rings such as, thiophene, furan, oxadiazoles, due to their relatively lower aromatic stabilization energy than benzene are reported to provide more effective p-conjugation between D and A, resulting in larger nonlinearities.

Azole derivatives containing a trivalent nitrogen (e.g., pyrrole, imidazole, pyrazole, 1,2,4-triazole, etc.) provide an additional potential bonding site. In these systems, attachment of substituents to both the trivalent nitrogen and an appropriate ring carbon can provide a fully conjugated system utilizing the nitrogen unshared electron pair. Under these circumstances, the heterocyclic ring itself also becomes a significant electron-donating substituent (Bouchet et al., 1974). The pyrazole ring system is a thermally and oxidatively stable, quasi-aromatic representative of the broader general class of five-membered heterocyclic azole derivatives (Elguero, 1984). From the literature, it is apparent that by all theoretical and experimental criteria, pyrazole derivatives possess the enhanced stability normally associated with the aromatic character. Keeping view of these, we have synthesized pyrazoles containing aromatic rings, with the aim of enhancing its nonlinear optical properties.

2. Experimental

2.1. Materials and methods

All the chemical reagents and solvents were of analytical grade and were purchased commercially and used without further purification. Melting point was recorded in °C and was measured using an Electrothermal melting point apparatus. Infrared spectra were recorded by using FTS 165 FT-IR spectrophotometer. Ultraviolet–Visible (UV–Vis) absorption spectra were recorded using a SPECORD S 100 (Analytikjena). The ^{1}H NMR spectra were recorded on 300 MHz Bruker FTNMR Ultra Shield TM spectrometer in $CDCl_3$ + DMSO-d_6 with TMS as the internal standard.

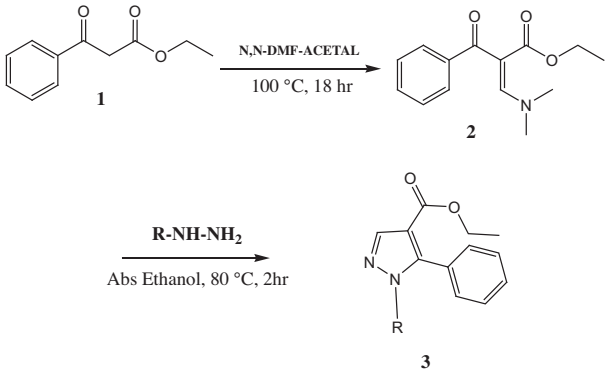
2.2. Synthesis

2.2.1. Synthesis of ethyl-3-(dimethylamino)-2-(phenylcarbonyl)prop-2-enoate (2)

A mixture of ethylbenzoylacetate (**1**) (10 g, 0.0520 mol) and *N*,*N*-dimethyl formamide dimethyl acetal (30.9 g, 0.26 mol) was heated to reflux for 18 h on an oil bath. The excess of acetal was distilled off under reduced pressure and the residue was purified by column chromatography using 60–120 silica gel mesh size using chloroform and methanol as an eluent to give a yellow solid (**2**) (11 g, 85%) with melting point 67–70 °C.

2.2.2. General procedure for preparation of different substituted pyrazole derivatives (3a–f)

To a solution of ethyl-3-(dimethylamino)-2-(phenylcarbonyl) prop-2-enoate (**2**) (1.0 equiv.) in a different series of aromatic/aliphatic hydrazine's (1.1 equiv.) was refluxed with absolute ethanol (10 ml) for 2 h, evaporated under reduced pressure. The residue was washed with 1.5 M HCl and the solid separated was filtered. The crude product was recrystallised using cold ethanol to afford different *N*-substituted-5-phenyl-1-pyrazole-4-ethylcarboxylate as a white crystalline solid (**3a–f**) (Giulia et al., 2008). Synthetic route for the same has been presented in Scheme 1. Characterization and spectral data of the newly synthesized compounds has been presented in Tables 1 and 2, respectively.



R= *tert* Butyl, Phenyl, 4-benzoic acid, 4-methyl phenyl, 2-bromo phenyl, 4-*tert* butyl phenyl.

Scheme 1 Synthesis of new pyrazole derivatives **(3a-f)**.

Table 1 Characterization data for new pyrazole derivatives.

Comp. No.	R	Melting point (°C)	Yield (%)	Mol. formula	Elemental analysis, found (calcd.)		
					C	H	N
3a	*tert*-Butyl	135	88	$C_{16}H_{20}N_2O_2$	70.65 (70.56)	7.35 (7.40)	10.33 (10.29)
3b	Phenyl	150	95	$C_{18}H_{16}N_2O_2$	74.00 (73.95)	5.48 (5.52)	9.40 (9.58)
3c	4-Benzoic acid	200	87	$C_{19}H_{16}N_2O_4$	67.66 (67.85)	4.88 (4.79)	8.56 (8.33)
3d	4-Methyl phenyl	135	85	$C_{19}H_{18}N_2O_2$	74.60 (74.49)	6.00 (5.92)	9.23 (9.14)
3e	2-Bromo phenyl	180	89	$C_{18}H_{15}BrN_2O_2$	58.55 (58.24)	4.15 (4.07)	7.62 (7.55)
3f	4-*tert* Butyl phenyl	170	90	$C_{22}H_{24}N_2O_2$	75.63 (75.83)	7.00 (6.94)	7.95 (8.04)

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