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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.

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.

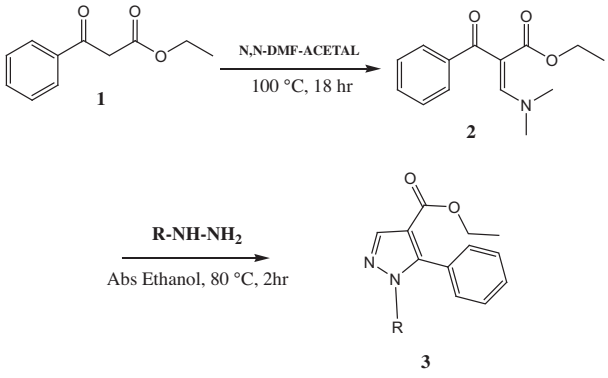
2.2. Synthesis

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)

Table 2 Spectral data for compounds.

Comp. No.	NMR ($CDCl_3$ + DMSO-d_6) (ppm)	IR($CHCl_3$) C═N, C═C (cm^{-1})	MS (*m*/*z* value) (*M* + 1)
3a	7.88 (s, 1H), 7.46–7.40 (m, 3H), 7.34–7.31 (m, 2H), 3.93 (q, 2H), 1.35 (s, 9H), 0.94–0.90 (t, 3H)	1615, 1540	272.3
3b	7.7 (s, 1H), 7.48–7.34 (d, 2H), 7.3–7.22 (m, 8H), 4.29 (q, 2H), 1.30 (t, 3H)	1600, 1555	292.3
3c	13.13 (s, 1H), 8.23 (s, 1H), 7.88–7.86 (d, 2H) 7.43–7.28 (m, 7H), 4.13–4.08 (q, 2H), 1.12–1.08 (t, 3H)	1678, 1550	336.3
3d	7.72 (s, 1H), 7.45–7.40 (d, 2H), 7.32–7.29 (m, 2H), 7.10–7.0 (m, 5H), 4.2–4.12 (q, 2H), 2.3 (s, 3H), 1.10–1.0 (t, 3H)	1620, 1532	306.1
3e	7.76 (s, 1H), 7.88–7.8 (d, 2H), 7.43–7.2 (m, 7H), 4.13–4.01 (q, 2H), 1.2–1.05 (t, 3H)	1635, 1540	371.2
3f	8.1 (s, 1H), 7.48 (d, 2H), 7.32–7.2 (m, 7H), 4.29 (q, 2H), 1.3 (9H, s), 1.3 (t, 3H)	1620, 1565	348.4

3. Results and discussion

3.1. UV–Vis spectroscopy

The UV–Vis absorption spectra were made using methanol in the wavelength range of 200–800 nm. The UV–Vis spectra of compounds **3a–f** in methanol showed absorption bands between 250 and 275 nm. All the measured compounds **3a–f** showed the absorption maximum in the 250–275 nm, which is ascribed to the pyrazole ring. The UV–Vis absorption spectra of compounds **3c** and **3e** are shown in Figs. 1 and 2.

3.2. FT-IR spectroscopy

FT-IR spectra of compounds **3a–f** have been investigated in the frequency range 400–4000 cm^{-1}. From the FT-IR analysis, it was found that the peaks observed at 1600–1678 and 1532–1565 cm^{-1} were numbers pertaining to the C═N and C═C of the synthesized compounds.

3.3. NMR spectroscopy

^{1}H NMR spectra were recorded on a Perkin-Elmer EM 300 MHz spectrometer using TMS as internal standard. The values for all the samples were presented in Table 2. Figs. 3 and 4 represents the ^{1}H NMR spectra of compounds **3a** and **3c**, respectively.

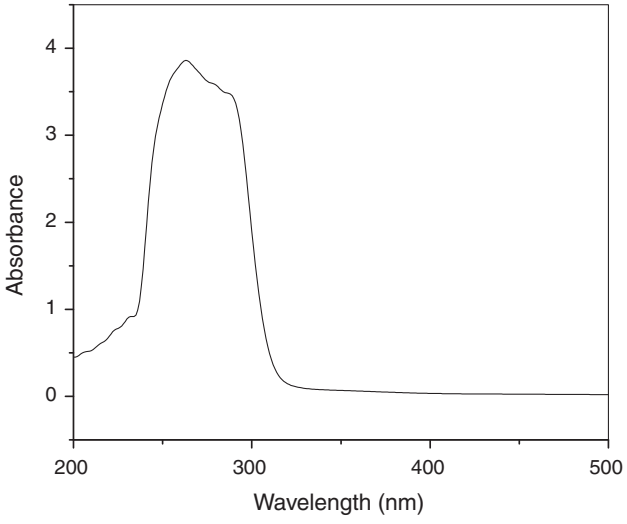


Figure 1 UV–Vis spectrum of compound **3c**.

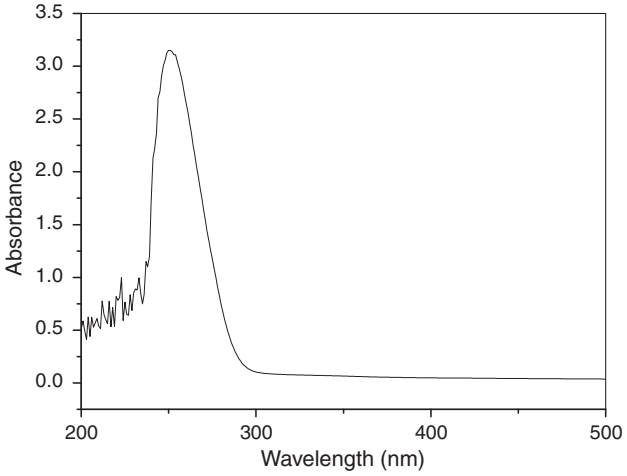


Figure 2 UV–Vis spectrum of compound **3e**.

4. Nonlinear optical properties

For measuring the optical nonlinearity of the compounds, 5 ns laser pulses at 532 nm, of 200 μJ energy were used. The technique of open aperture *z*-scan was employed to determine the nonlinear absorption of the samples (Sheik-Bahae et al., 1990). In this experiment a laser beam is first focused using a lens, and the direction of beam propagation is taken as the *z*-axis. The *z*-value increases toward either side of the focal point, but the sign will be negative on one side and positive on the other (similar to a number line). The sample is now placed in the beam at a position (*z*) between the lens and the focal point, and the transmitted energy is measured. Then the sample is moved in small steps toward the focus and beyond, and the transmission is measured at each step. At each of these positions the sample will see a different laser fluence (energy/beam area), which will be a maximum at the focus. Thus in practice the open aperture *z*-scan is essentially a sample transmission measurement, the data being continuously taken while the sample is slowly translated from a position before the focus to a position after the focus. The graph plotted between position *z* and the normalized transmittance of the

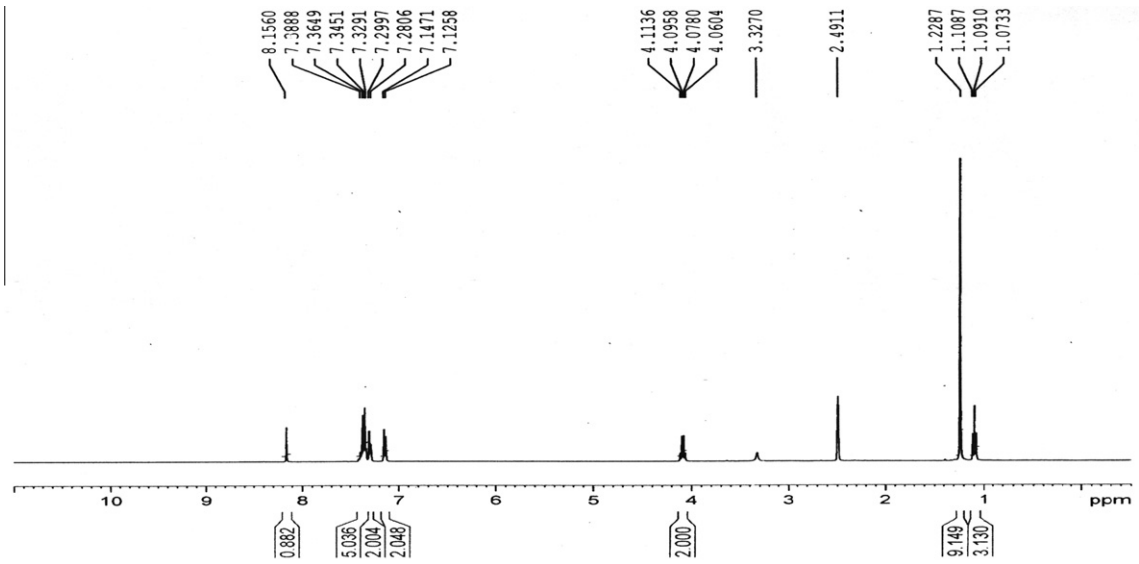


Figure 3 NMR spectrum of sample **3a**.

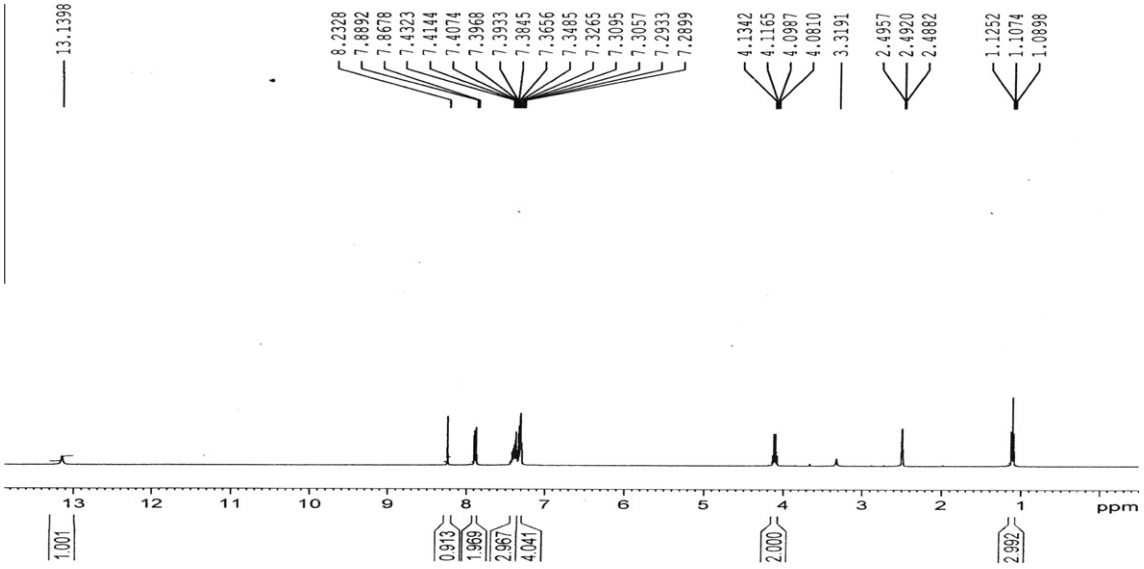


Figure 4 NMR spectrum of sample **3c**.

sample is known as the open-aperture z-scan curve. This graph will reveal the nature of the absorptive nonlinearity in the system.

If a spatially Gaussian laser beam is used, then each z-position will correspond to an input laser energy density (fluence) of $4(\ln 2)^{1/2}E_{in}/\pi^{3/2}\omega(z)^2$, where E_{in} is the input laser pulse energy and $\omega(z)$ is the beam radius. $\omega(z)$ is given by $\omega(0) * [1 + (z/z_0)^2]^{1/2}$, where $\omega(0)$ is the beam radius at the focus and $z_0 = \pi\omega(0)^2/\lambda$ is the Rayleigh range (diffraction length), where λ is the excitation wavelength. Thus from the open aperture z-scan data it is possible to draw a graph between the input laser fluence and the sample transmission, which is known as the nonlinear transmission curve.

In our experiment a planoconvex lens of 20 cm focal length was used to focus the laser, and the focal spot radius was about 18 μm. All compounds were dissolved in chloroform. Sample solutions were taken in a 1 mm thick glass cuvette, (Hellma GmBH) which was mounted on a programmable linear translation stage. The samples had a linear transmission of 80% at the excitation wavelength. The input energy reaching the sample and the energy transmitted by the sample were measured using two pyroelectric energy probes (RjP 735, Laser Probe Inc.). The interval between successive laser pulses was kept sufficiently large (about 1 s) to allow for complete thermal relaxation of the sample between adjacent laser pulses. The experiment was automated using a Labview program running in the Windows XP Environment.

Even though all compounds exhibited nonlinear absorption to various degrees, reliable data was obtained only in compounds **3a** and **3e**. Results for these compounds are shown

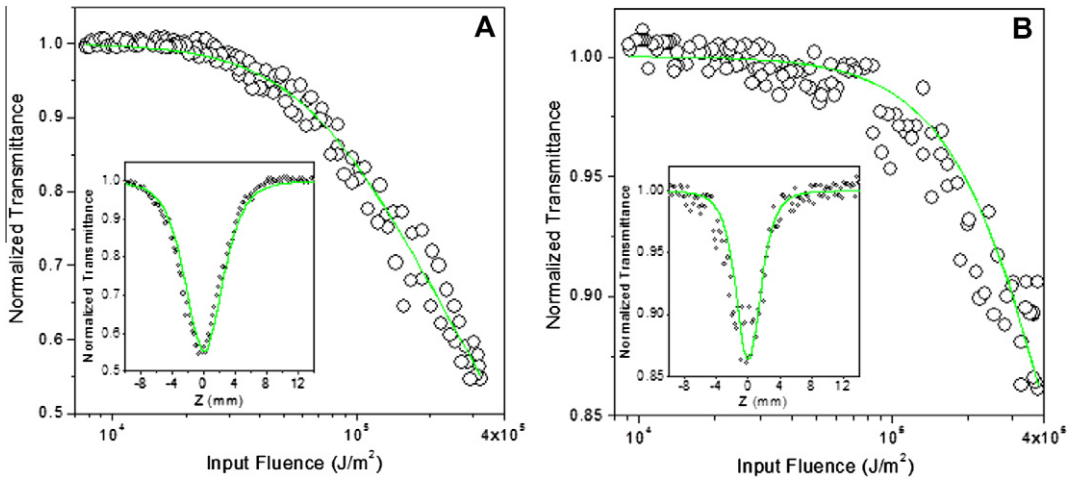


Figure 5 Nonlinear absorption in chloroform solution of (A) compound **3c** and (B) compound **3e** at an excitation wavelength of 532 nm, using 5 ns laser pulses. The open aperture *z*-scans are shown in the insets. Circles are measured data points while solid curves are numerical fits to the data according to Eq. (1).

in Fig. 5(A) and (B), respectively. Upon trying different nonlinear transmission equations, the open-aperture *z*-scan data is found to fit well to a three-photon type absorption (3PA) given by the equation (Sutherland, 1996)

$$T = \frac{(1-R)^2 \exp(-\alpha L)}{\sqrt{\pi} p_0} \times \int_{-\infty}^{\infty} \ln\left[\sqrt{1+p_0^2 \exp(-2\tau^2)} + p_0 \exp(-\tau^2)\right] d\tau \qquad (1)$$

where T is the measured transmission of the sample, L and R are the sample length and surface reflectivity, respectively, and α is the linear absorption coefficient. p_0 in Eq. (1) is given by $p_0 = \sqrt{2\gamma(1-R)^2 I_0^2 L'_{\text{eff}}}$, where I_0 is the on-axis peak intensity, L'_{eff} is given by $[1-\exp(-2\alpha L)]/2\alpha$, and γ is the three-photon absorption coefficient.

In reality, rather than genuine 3PA involving virtual energy levels as intermediate states, a more probable mechanism herein is sequential three-photon absorption involving real levels as intermediate states. Therefore, the effect is an ''effective'' 3PA process. From Fig. 4, the numerically calculated effective three-photon absorption coefficients (γ) are 5×10^{-24} m^3/W^2 and 2.6×10^{-25} m^3/W^2, respectively, for compounds **3** and **5**. To put this in perspective, the γ values obtained recently for Bi and Na doped ZnO nanoparticle dispersions under similar excitation conditions are in the order of 10^{-24} m^3/W^2 (Karthikeyan et al., 2009a) and 10^{-25} m^3/W^2 (Karthikeyan et al., 2009b), respectively. Obviously the present samples show an optical limiting behavior at the higher input laser fluencies, indicating the potential application of these materials in photonics devices.

5. Conclusions

The optical nonlinearity of the synthesized compounds 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 a carboxylic acid group and ester substituent shows the maximum nonlinear absorption. Compound **3e** also shows nonlinearity, which is lower in magnitude compared to compound **3c**. From the measurements we conclude that these two compounds are potential candidates for optical limiting applications.

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