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Research paper

Linear and femtosecond nonlinear optical properties of soluble pyrrolo[1,2-a] quinoxalines

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HIGHLIGHTS

- Third order nonlinear optical properties were studied for novel quinoxalines molecules.
- Linear optical properties were investigated using TD-DFT calculations and absorption spectroscopy.
- The highest values for $\chi^{(3)}$, χ & n_2 are obtained for the PQ-a derivative.
- $\chi^{(3)} = 4.35 \times 10^{-14}$ esu, $\chi = 4.41 \times 10^{-31}$ esu, and $n_2 = 8.44 \times 10^{-16}$ cm^2/W.

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Femtosecond
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Third order nonlinearity

ABSTRACT

We report our results from the investigations of linear and ultrafast nonlinear optical properties of a set of pyrrolo[1,2-a]quinoxalines. Using the steady state optical techniques and density functional theory calculations the linear optical properties were investigated while the non-resonant ultrafast nonlinear optical properties were studied using the degenerate four-wave mixing technique at a wavelength of 800 nm with 70 fs pulses. The investigated molecules demonstrated large off-resonant second hyperpolarizability (γ) and nonlinear refractive index (n_2) values compared to similar molecular moieties with potential application in optical devices.

1. Introduction

Quinoxalines [1,2], belonging to the family of nitrogen containing heterocycles, are well known class of fluorescent compounds and possessing high quantum yields finding potential applications in organic semiconductors, dyes and chemically controllable switches [3–5]. These kind of organic luminophores possess some significant properties such as color purity, photostability and easy synthesis access [6]. Moreover, fluorophores containing a hererocyclic system are potentially useful in biological activities and for diagnostic methods [7–9]. It is well known that Quinoxaline itself being a weak base, its characteristics can be controlled by modifying the type and location of substituents. Quinoxalines with different substitutions have been utilized as fluorescence probes in various complex chemosensors [10,11], biological [12,13], optoelectronic [14–16] and photonic devices [17,18]. Although the presence of delocalized π-electron distribution in these molecules is expected to invoke strong nonlinear optical (NLO) properties, there is acute paucity in the existing literature, which discuss and present the NLO properties/coefficients of Quinoxalines. Recently, Kalinin et al. [19] presented large quadratic NLO activity of chromophores with divinylquinoxaline conjugated π-bridge. Another report [20] theoretically predicted a good quadratic NLO response of chromophores with 3,7-divinylquinoxalin-2-one π-electron bridge. On the other hand, investigations focusing on the third order NLO properties of these classes of molecules were never undertaken. Recently we reported [21] the synthesis and luminescence properties of few pyrrolo [1, 2-a]quinoxaline derivatives. In this letter, we present our studies on the linear and ultrafast NLO properties of these molecules (referred to as PQ-a) and its derivatives with different functional group substitution in solution employing the DFWM technique in box-car geometry with non-resonant excitation at a wavelength of 800 nm and utilizing ~70 fs pulses. The third order susceptibility ($\chi^{(3)}$), second hyper-polarizability (γ) and nonlinear refractive index value (n_2) for these molecules were

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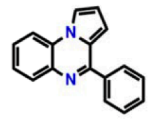
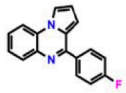
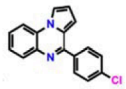
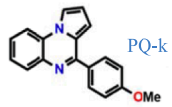
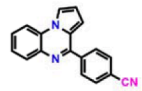
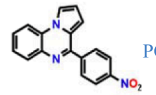
Table 1
Structures of quinoxalines used in the NLO study.

Pyrrolo[1,2-a] quinoxaline	Pyrrolo[1,2-a] quinoxaline with halogen substituents	Pyrrolo[1,2-a]quinoxaline with electron donating group	Pyrrolo[1,2-a]quinoxaline with electron-withdrawing group
 PQ-a	 PQ-d  PQ-e	 PQ-k	 PQ-m  PQ-n

estimated with the best value of 4.35×10^{-14} esu, 4.41×10^{-31} esu, and 8.44×10^{-16} cm^2/W, respectively, was obtained for the PQ-a derivative.

2. Experimental details

The pyrrolo[1,2-a]quinoxaline (PQ-a) bearing halogen substitutions (4-F, 2-Cl) referred to as PQ-d and PQ-e, were synthesized on reaction with arylacetic acids with corresponding functional groups. Electron withdrawing groups [–CN] and [$–NO_2$] referred to as PQ-m and PQ-n respectively were substituted on the reaction of arylacetic acids with corresponding functional groups with 1-(2-aminophenyl)-pyrrole. Whereas the pyrrolo[1,2-a]quioxalines with electron donating group [-OMe] referred to as PQ-k was prepared in reaction of arylacetic acids with the corresponding electron-donating group. Detailed synthesis procedures of these reactions are reported in literature [21]. The details of molecular structures are presented in Table 1.

Ultrashort laser pulses used for DFWM measurements are obtained from a commercial Ti:Sapphire regenerative amplifier delivering 1 kHz, ~1 mJ pulses at a central wavelength of 800 nm and a duration of ~70 fs were used for the DFWM measurements. DFWM experimental set-up was configured in the standard forward phase matching geometry (box-car) as illustrated in Fig. 1(a) [22–24]. The fundamental beam was divided into three nearly equal intensity beams and the spatial positions of the beams are such that they form three corners of a square and are focused into the sample solution using a plano convex lens of focal length 20 cm. The carefully maintained phase matching condition take cares that on the focal spot the phases of the three beams are identical in time. The resultant DFWM signal was detected at the fourth corner of the box using a photodiode interfaced to lock-in amplifier. This fourth beam was generated because of the interaction $\mathbf{k_4} = \mathbf{k_3} - \mathbf{k_2} + \mathbf{k_1}$ as described in the Fig. 1(b). The molecules were dissolved in DMF solvent and the DFWM measurements were performed for 0.1 mM solutions in 3 mm quartz cuvettes.

3. Results and discussion

3.1. Linear optical properties

Absorption spectra of all the molecules were recorded in DMF solvent on a Cary 5000 UV–VIS-NIR spectrophotometer. All the pyrrolo [1,2-a] quinoxaline molecules shows absorption in visible region ranging from 350–385 nm (Fig. 2). To get insights in to the observed absorption maxima, DFT/TDDFT calculations have been performed for these molecules. All the theoretical calculations have been carried using Gaussian 09 software [25]. The molecules are fully optimized using B3LYP functional with 6-31G (d,p) basis set. Further, optimized molecules are without imaginary frequency and, hence, are at their lowest energy state.

To calculate the linear optical properties (electronic excitations) in a molecule, TDDFT calculations has been carried out at same level of theory. From the data presented in Table 2 it is observed that there is a good agreement between experimental and TDDFT calculated absorption energies. The experimental absorption for an un-substituted pyrrolo[1,2-a]quinoxalines i.e. PQ-a is 352 nm and calculated absorption is at 348 nm and the transition is from HOMO → LUMO. However there is not much change in absorption on addition of halogen (F or Cl) substituent to pyrrolo[1,2-a]quinoxaline. For molecules PQ-d and PQ-e, measured absorptions were at 354 nm and 349 nm, respectively. TDDFT results reproduced the experimental results and shows absorption at 347 nm (PQ-d) and 353 nm (PQ-e) and both arise due to the HOMO → LUMO transitions. Further on adding electron donating methoxy group ($–OCH_3$) to benzene, i.e. for molecule PQ-k, there is no appreciable change in the wavelength. The observed and calculated wavelength for PQ-k is at 353 nm and 346 nm, respectively. But on addition of strong electron withdrawing group such as cyano (PQ-m) and nitro (PQ-n) group, a red shift in the absorption was observed. For PQ-m, 15 nm bathochromic shift was observed and its absorption maxima is at 363 nm while TDDFT results depict absorption at 378 nm which is also

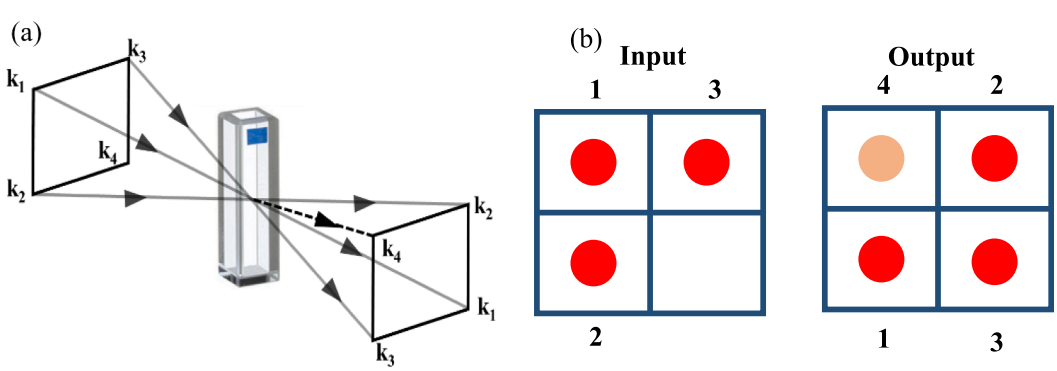


Fig. 1. (a) Schematic of the box-car DFWM set-up. Beams 1–3 are coincident on the solution. The resultant, fourth beam (dotted line) is the DFWM signal (b) three beam position in input along with the fourth beam in output.

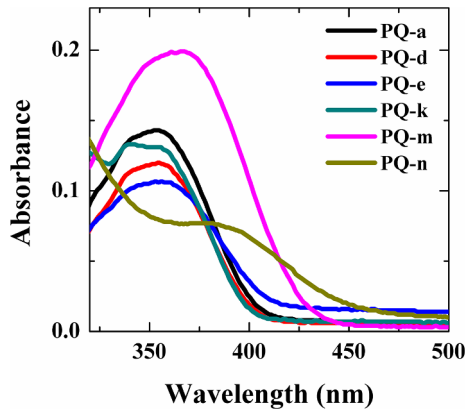


Fig. 2. Absorption spectra of the quinoxalines used in the present study.

Table 2
Measured absorption maxima (λ_{exp} in nm), calculated absorption energies (λ_{cal} in nm), oscillator strength (*f*), major transitions (MT) and % weight (%Ci) calculated at TD-B3LYP with 6-31G (d,p) basis set.

Name	λ_{exp}	λ_{cal}	*f*	MT	%Ci
PQ-a	352	348	0.177	H → L	93
PQ-d	354	347	0.186	H → L	93
PQ-e	349	353	0.188	H → L	93
PQ-k	353	346	0.263	H → L	93
PQ-m	363	378	0.158	H → L	95
PQ-n	382	429	0.102	H → L	98

due to HOMO → LUMO transitions. Molecule PQ-n, where substitution was with NO_2, shows almost 30 nm red shift in absorption. The experimental and calculated absorption for PQ-n are at 382 nm and 429 nm, respectively. It is evident that there is no change in absorption of molecule on addition of electron donating group while red shift in absorption was observed with electron withdrawing group. Also from TDDFT results for all molecules the major transition is from HOMO → LUMO and corresponding HOMO/ LUMO molecular orbital pictures are shown in Fig. 3. The absorption maxima for all the molecules are in the range of 349–380 nm and corresponding spectra of these compounds are shown in Fig. 2 and the values of the absorption maxima are tabulated in Table 2.

3.2. Third order nonlinear optical properties

DFWM is one of the most important and versatile techniques to characterize the third order NLO properties of different materials such as organic-semiconductors, nanomaterials etc. When two or more waves interact in a nonlinear medium to produce an output at various sum or difference frequencies, it refers to the interaction of four waves via the third order nonlinear polarization. When all waves have the same frequency, the process is called degenerate, although their wave vectors are different. In this process, three coherent beams incident on a nonlinear medium generate a fourth beam due to the third order nonlinearity. The strength of this fourth beam is dependent on a coupling constant that is proportional to effective $\chi^{(3)}$ and measurement on 4th signal will yield information about the $\chi^{(3)}$ tensor component of the medium [24,26–28]. Second hyperpolarizability [γ] and nonlinear refractive index [n_2] can be calculated from these value of $\chi^{(3)}$ components [23]. The third-order NLO susceptibility $\chi^{(3)}$ was estimated by comparing the measured DFWM signal of the sample with that of CCl_4 as reference with $\chi^{(3)} = 4.4 \times 10^{-14}$ esu [24] and $n_2 \approx 5.0 \times 10^{-16}$ cm^2/W [29], and it is given by the following relationship [23]:

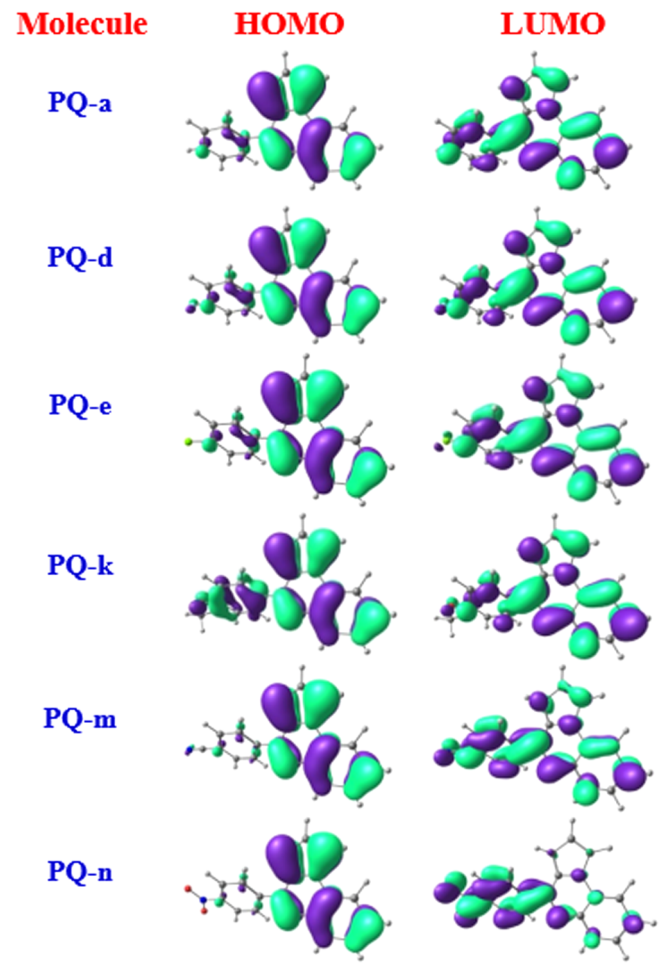


Fig. 3. HOMO, LUMO molecular orbitals of the molecules investigated in this study.

$$\chi^3_{sample} = \left(\frac{n_{sample}}{n_{ref}}\right)^2 \left(\frac{I_{sample}}{I_{ref}}\right)^{\frac{1}{2}} \left(\frac{L_{ref}}{L_{sample}}\right) \times \alpha L_{sample} \times \left(\frac{e^{\frac{\alpha L_{sample}}{2}}}{1 - e^{-\alpha L_{smaple}}}\right) \times \chi^3_{ref},$$

where *I* is the DFWM signal intensity, α is the linear absorption coefficient, L is the sample length, and n is the refractive index. We estimated the magnitude of $\chi^{(3)}_{1111}$ by maintaining the same polarization for all the three beams. The input power of the three mixing pulses were chosen such that the effect of nonlinear absorption was minimal. The measured $\chi^{(3)}$ at these intensities are, therefore, real without any imaginary component due to multi-photon absorption. The choice of low input intensities allowed us to neglect the higher order non-linearities. To estimate the second-order hyperpolarizability, γ the following relation has been used [23]: $\gamma_{sample} = \frac{\chi^3}{T^4 N_0}$, where N_0 is the number density of the molecules per milliliter, and $T = (n^2_{sample} + 2)/3$ is the local field factor. Since all the samples had negligible linear absorption at the working wavelength of 800 nm we expect the measured $\chi^{(3)}$ and γ values to be off-resonant. The non-linear refractive index n_2 is estimated from the calculated $\chi^{(3)}$ using the following relation: $n_2(\text{cm}^2/\text{W}) = \left(\frac{0.0395}{n_0^2}\right)\chi^{(3)}(\text{esu})$, where n_0 is the linear refractive index of the solution. The experimentally measured $\chi^{(3)}$, γ and n_2 for the molecules are reported in Table 3. The estimated values for third order nonlinear susceptibility ($\chi^{(3)}$) varied in the range of $2.95 \times 10^{-14} - 4.35 \times 10^{-14}$ esu, second-order hyperpolarizability (γ) from $2.99 \times 10^{-31} - 4.41 \times 10^{-31}$ esu and the non-linear refractive index (n_2) between $5.73 \times 10^{-16} - 8.44 \times 10^{-16}$ cm^2/W with the best functionality obtained with the PQ-a derivative.

The intensity dependence of the DFWM signal amplitude for these

Table 3
Third order nonlinear coefficients of the quinoxaline molecules considered in the study.

Sample	$\chi^{(3)}$(esu)	γ (esu)	n_2 (cm^2/W)
PQ-a	4.35×10^{-14}	4.41×10^{-31}	8.44×10^{-16}
PQ-d	3.52×10^{-14}	3.57×10^{-31}	6.82×10^{-16}
PQ-e	4.23×10^{-14}	4.29×10^{-31}	8.20×10^{-16}
PQ-k	3.60×10^{-14}	3.66×10^{-31}	6.99×10^{-16}
PQ-m	2.95×10^{-14}	2.99×10^{-31}	5.73×10^{-16}
PQ-n	3.44×10^{-14}	3.49×10^{-31}	6.68×10^{-16}

samples are shown in Fig. 4(a)–(f), respectively. At relatively low input light intensities the DFWM signal amplitude follows a dependence that is essentially cubic. This indicated that within low intensity range the nonlinearity behaves in an essentially Kerr-like manner; that is, there is no clear indication of the necessity for introducing a fifth-order correction. For higher intensities DFWM signal saturation has been observed.

The non-resonant NLO coefficients using femtosecond laser pulse excitation obtained for these quinoxalines molecules were found to be competent among the reported values for similar molecular moieties. Prabhakar et al. reported off-resonant γ values of $\sim 10^{-32}$ esu for croconate dyes using DFWM measurements with 100 fs pulses [30]. Li et al. reported γ values of $\sim 10^{-31}$esu for squaraines. [31]. Huang et al. reported off-resonant non-linearities of dihydroxy phosphorus (V) tetrabenzotriazacoroles in the range of 10^{-31} esu [32]. Tran et al. reported γ values of the order of 10^{-32} esu for squaraine dyes near 700 nm [33]. From this studies it is apparent that our molecules possess better or similar values obtained for γ. The n_2 values of these molecules are much higher than that of the solvent. Therefore, they can find applications in optical switching. Further, the nonlinear absorption studies of these molecules will be taken up at a later stage and if reverse saturable absorption is observed, they find applications in optical limiting while saturable absorption kind of nonlinear absorption can be utilized for mode locking applications. Specific to NLO investigations on quinoxalines molecules, Kalinin et al. [19], Levitskaya et al. [20] and Liu et al. [34], studied novel chromophores with quinoxaline moieties and theoretically predicted NLO characteristics. Therefore, the presented third order NLO studies for the quinolxaline molecules are encouraging and is expected to provide impetus for further development of quinoxaline based molecules with better NLO responses. Furthermore, such detailed structure-property studies will help us in understanding the design principles for synthesizing molecules with strong nonlinear refraction and/or nonlinear absorption.

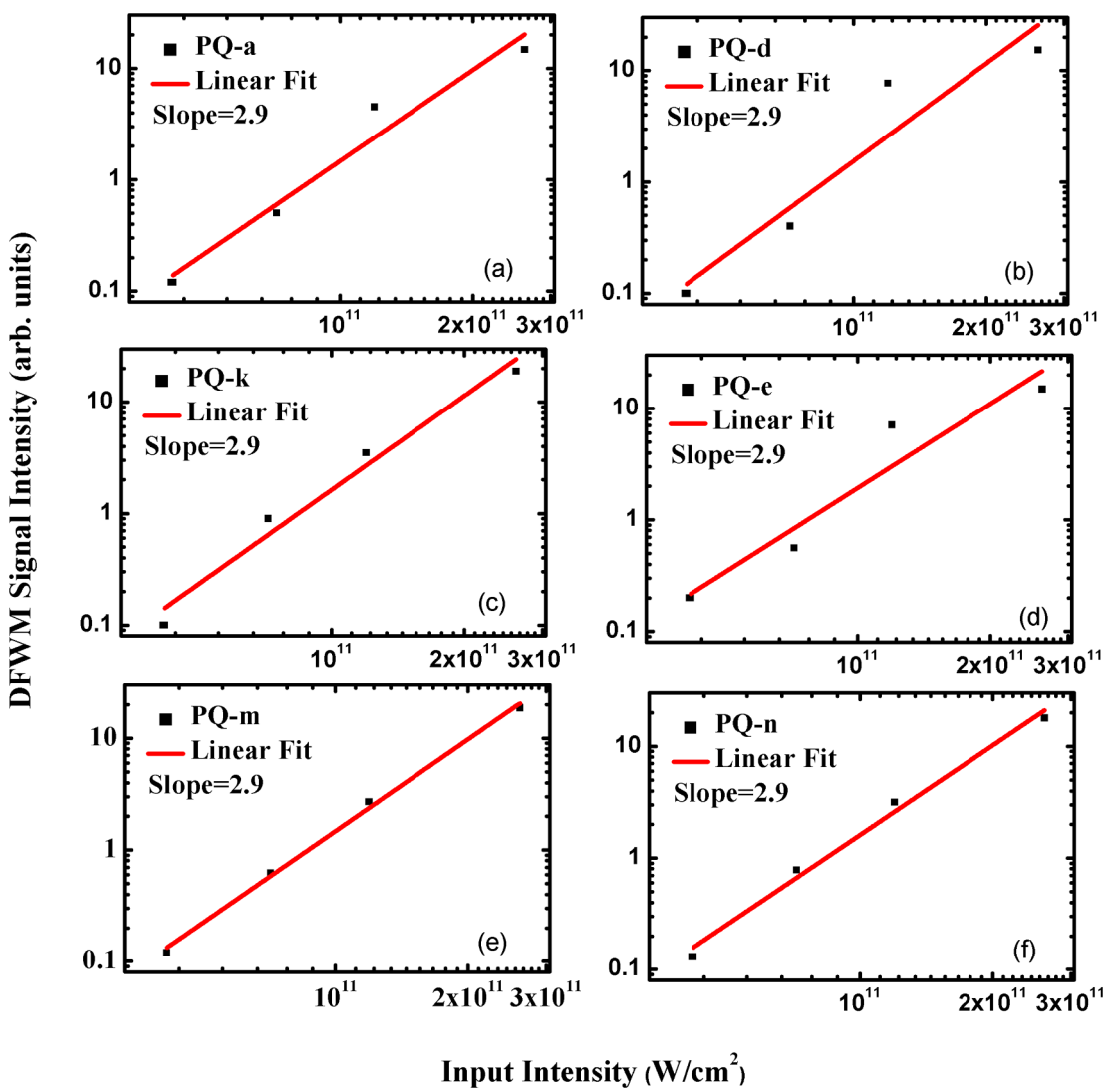


Fig. 4. Plots showing the cubic dependence for: (a) PQ-a; (b) and (d) for PQ-a with halogen substitute; (c) for PQ-a with electron donating group; (e) and (f) for PQ-a with electron withdrawing group.

4. Conclusions

We have investigated the linear and femtosecond nonlinear optical properties of a few quinoxalines. These molecules are having absorption in visible region (from 349 to 380 nm in DMF solvent). The nonlinear optical response of these molecules are measured in the femtosecond regime using the DFWM technique. The crucial nonlinear optical property of the material is the nonlinear response to an electric field given by the macroscopic third-order optical susceptibility $\chi^{(3)}$. The corresponding microscopic third order nonlinear optical property is the molecular second hyperpolarizability γ, and suitable candidates for optical components usually have larger values of γ. Our measurements establish that the pyrrolo[1,2-a]quinoxalines with different functional groups having specific electronic behaviour and thus attributing to the possibility of tuning the γ value for application requirement. In additional to their proven excellent fluorescence properties the presented non-linear characteristics of these molecules show potential for optoelectronic and all-optical switching applications.

Declaration of Competing Interest

The authors declare that there are no known conflicts of interest.

Acknowledgments

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