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DMRG method reveals that third harmonic generation coefficients (γ) of Indeno[2,1-b]fluorene and its structural isomers correlate with their diradical character.

Linear and Nonlinear Optical Properties of Indeno[2,1-b]fluorene and its Structural Isomers

Simil Thomas,[a] and Kwang S. Kim[*a]

Linear and non-linear optical properties of indeno[2,1-b]fluorene (**1**) and its structural isomers with 20 π-electrons have been studied using many body methods. As compared to other π electron systems of similar conjugation length, experimentally measured optical gap (vertical excitation energy) and singlet-triplet gap of **1** are quite small. The diradical character calculated using ab initio density matrix renormalization group (DMRG) of **1** is the largest among its isomers, which explains its lowest singlet-triplet gap. The optical gaps calculated by the DMRG method, employing long-range interacting Pariser-Parr-Pople model show good agreements with the experimental values as compared to those calculated by DFT, MP2, and CASPT2 methods. Using correlated Hamiltonian and DMRG approach, the third harmonic generation coefficient is found to correlate well with the diradical character.

1 Introduction

A diradical is a molecular system with two unpaired electrons, each of which can occupy two degenerate or nearly degenerate molecular orbitals.[1] Most of the diradicals are very reactive and short lived because of the singly occupied molecular orbitals. However, several stable diradicals have been reported by several groups.[2–7] Recently, diradicals have been widely investigated in the context of its singlet fission to enhance the efficiency of organic solar cells.

Conjugated π-networks play an important role to propagate the donor-acceptor properties of various substituents. They have large second order polarizability $\chi^{(2)}$, large third order polarizability $\chi^{(3)}$, which can manifest as third harmonic generation (THG) and two-photon absorption (TPA) cross sections. One of the interesting aspect of conjugated molecules is their nonlinear optical (NLO) responses that can be tuned by substitution. There exist a number of molecules with large third harmonic generation coefficients (γ), compared to molecules with large second harmonic generation coefficients (β), because β vanishes in molecules having inversion symmetry. Also, γ is significantly affected by the delocalization length and dimensionality of the system. Correlated models give a power-law variation of $\chi^{(3)}$ against conjugation length with an exponent which is smaller than that given by the free-electron models.[8–10] Materials with large NLO responses have been used in ultra-fast optical signal processing,[11] 3D optical data storage,[12] optical computing,[13] harmonic generators,[14] frequency mixing,[15] and optical switching.[16,17]

One of the approaches for enhancing the NLO response of conjugated molecular systems is to increase the conjugation

length. There have been other approaches like bond length alternation[18] for designing molecular systems with large NLO responses.[19,20] Recently Nakano *et al.* reported that static third order NLO responses of a material[21,22] has a strong effect on diradical character. After this report, there had been an extensive study on diradical systems. Nakano *et al.* showed that molecules with intermediate diradical character have large $\chi^{(3)}$.[23] It is also interesting to see large $\chi^{(3)}$ values reported for acenes and dicyclo-fuesd acenes.[24,25]

In diradicals, within one particle Hückel theory, the lowest singlet and triplet states are degenerate and the degeneracy of these levels can be removed by electron-electron interactions. Electron-electron interactions in conjugated systems are strong enough to alter the ordering of energy levels[26] and hence representation of such molecular system by a single determinant is difficult. Therefore, single determinant methods like DFT or Hartree-Fock (HF) are not good enough to correlate diradical nature and $\chi^{(3)}$. Hence it is better to use the semi-empirical Pariser-Parr-Pople (PPP) model Hamiltonian[27,28] approach to solve the problem. Since the system size that can be solved exactly is limited to a maximum of 16 lattice sites,[29] the basis set for the present study has to be truncated in order to solve the problem of large basis size. DMRG[30–32] is an efficient method to truncate unimportant basis sets in one-dimensional systems. Its efficiency and accuracy in one-dimensional and quasi one-dimensional systems is quite good even though it is less accurate in two-dimensional systems. Hence, we have used the DMRG method to study the linear and non-linear optical properties of diradical systems using the PPP Hamiltonian.[9,33]

A couple of recently synthesized molecules, indeno[2,1-b]fluorene and its structural isomers,[34] are used in the present study. All the above molecules have 20 π electrons and its structures are shown in Fig. 1. They can have some aromatic and radical nature. A commonly used method to calcu-

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late the diradical character of a system is the complete active space self-consistent field (CASSCF) method.[35,36] For conjugated systems, active space should contain all the π-electrons. Current implementation of CASSCF is limited to 16 active electrons.[37] But the system we considered consists of 20 π-electrons, which cannot be handled by the CAS method. The recently developed DMRG method can overcome this limitation and we performed the ab initio density matrix renormalization group method using BLOCK code.[38,39] Ab initio DMRG in the current case is same as common CASSCF method but without orbital optimization. Active space consists of 20 electrons and 20 low-lying π-orbitals. Exponential complexity of CAS method in long molecules is overthrown by the DMRG algorithm as implemented in the BLOCK code. This method is then used only to calculate the diradical character by diagonalizing the one-electron reduced density matrix (1-RDM) obtained from the BLOCK code for each of the molecules. In the next section, we briefly discuss the model Hamiltonian and the DMRG method used in our study. In the last section we present our results and discussions.
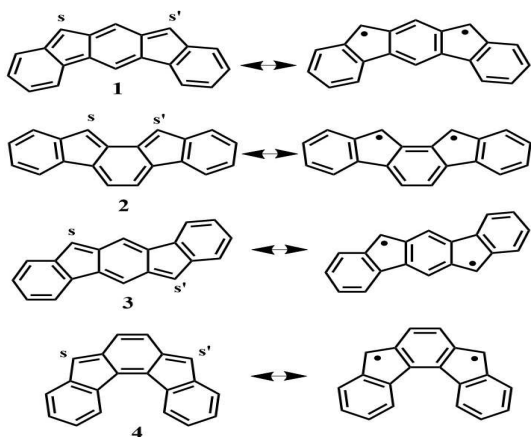
Fig. 1 Resonance structures of indeno[2,1-b]fluorene (**1**) and it structural isomers used in the present study. The geometry is optimized at the UB3LYP/6-311G* level and all the systems have 20 π electrons. Substituents attached at positions s and s' are modelled with a different site energy.

2 Methodology

2.1 Hamiltonian

We studied linear and nonlinear optical properties of diradical systems using the PPP model Hamiltonian,

$$H = \sum_i \varepsilon_i n_i - \sum_{<i,j>\sigma} t_{ij}(a^\dagger_{i\sigma}a_{j\sigma} + a^\dagger_{j\sigma}a_{i\sigma}) \quad (1)$$
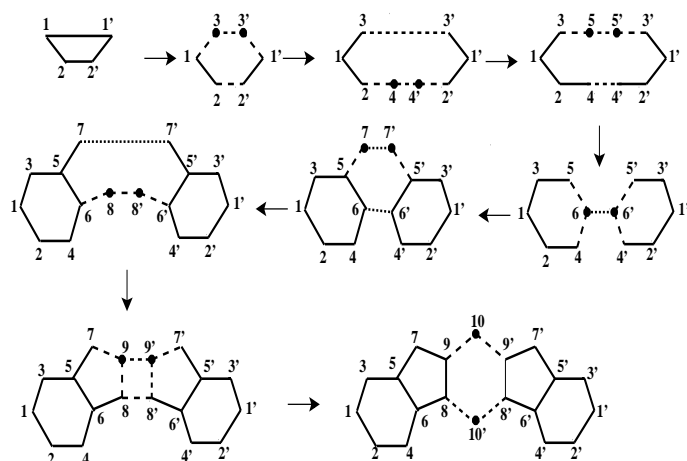$$+ \frac{U}{2}\sum_i n_i(n_i-1) + \sum_{i>j}V_{ij}(n_i-1)(n_j-1)$$

where $\hat{a}^\dagger_{i\sigma}$ ($\hat{a}_{i\sigma}$) creates (annihilates) an electron at site i with spin σ, and $\hat{n}_i$ is the number operator. Transfer integral t_{ij} between nearest neighbors are only retained and calculated using linear extrapolation $t_{ij} = t_0(1 - \frac{d_{ij}}{r_{ij}})$, where $t_0 = 2.4$ corresponds to C-C distance of 1.397 Å, $d_{ij} = r_{ij} - 1.397$ and r_{ij} is the distance (Å) between i and j sites. ε_i is the orbital energy (in eV) of the p_z orbital on the ith carbon atom. In an unsubstituted system, it is a good approximation to consider all carbon p_z orbitals in the same chemical environment and choose $\varepsilon_i = 0$. However in a donor/acceptor system, $\varepsilon_i > 0$ to simulate the substitution by electron pushing group and $\varepsilon_i < 0$ to simulate the substitution by electron pulling group in the system. To mimic the effect of the substitution, we have changed the site energies at the positions s and s' as shown in Figure 1 to take account of experimentally synthesized molecular structures where hydrogen atoms at above positions are substituted by groups like triisopropylsilyl, mesityl etc. U_is are on-site electron-electron interaction (11.26 eV for carbon) and the intersite electron-electron repulsions V_{ij}s are parametrized using the Ohno interpolation scheme[40]

$$V_{ij} = U(1 + 0.6117r_{ij}^2)^{-1/2}. \quad (2)$$

The PPP model with these standard parameters has been widely used for the successful modeling of the excited states of the conjugated systems. We have optimized the geometry using 6-311G* basis set and UB3LYP functional in density functional theory (DFT) method within Gaussian 09.[41] The optimized structure is used to calculate inter-site electron-electron interaction potential in PPP Hamiltonian and diradical character in ab initio DMRG method. The starting point in the DMRG scheme is a four membered ring. In the infinite scheme, two sites are added in the middle of the ring and the ring size is expanded till desired system size is reached (Fig. 2). Infinite DMRG calculations are done keeping 300 density matrix eigenvectors. After this finite DMRG sweeps is started, accuracy of the above calculations is further increased.

Finite sweep is continued until the energy eigenvalues converge within an accuracy of 10^{-2} eV and this requires 2 to 3 finite sweeps. For computation of dynamic NLO response coefficients, we use the standard perturbative theoretic approach introduced by Orr and Ward.[42] They express second order hyperpolarizability in terms of the eigenfunctions of the unperturbed Hamiltonian.

$$\gamma_{ijkl}(-\omega_1 - \omega_2 - \omega_3; \omega_1, \omega_2, \omega_3) = \hat{P}_I \sum_{mn\nu}$$
$$\frac{\mu^k_{g\nu}\mu^j_{\nu n}\mu^i_{nm}\mu^h_{mg}}{(\omega_{\nu g} - \omega_1 - \omega_2 - \omega_3)(\omega_{ng} - \omega_1 - \omega_2)(\omega_{mg} - \omega_1)}$$
$$(3)$$

Fig. 2 Infinite DMRG algorithm for constructing the molecule **1**. Starting size is a system of 4 sites and new sites added are shown as filled circles. Dotted lines are the new bonds introduced by the insertion of new sites. Sites with unprimed (primed) indices correspond to left-block (right-block).

where the operator $\hat{P}_I$ generates all permutations: $(-(\omega_1 + \omega_2 + \omega_3), i)$, (ω_1, j) and (ω_2, k), and (ω_3, l), leading to 24 terms for γ. $\mu_{nm}^i = \langle n|\mu^i|m \rangle$ is the ith component of the transition dipole moment between state n and m, ω_{vg} is the energy gap between the excited state v and ground state g. These expressions appear to require all the eigenvalues and eigenvectors of the Hamiltonian matrix. However, the correction vector (CV) method introduced by Ramasesha *et al.*[43,44] incorporates all the excitations in the chosen Hilbert space without explicitly computing the unperturbed excited states of the Hamiltonian. The CV technique is used to calculate THG coefficients.

In the CV method, the first and second order correction vector $|\phi_i^{(1)}(\omega_1)\rangle$ and $|\phi_{ij}^{(2)}(\omega_1, \omega_2)\rangle$ are computed by solving a set of linear algebraic equations defined by

$$(H_0 - E_0 + \hbar\omega)|\phi_i^{(1)}(\omega)\rangle = \tilde{\mu}_i|g\rangle \qquad (4)$$

$$(H_0 - E_0 + \hbar\omega_2)|\phi_{ji}^{(2)}(\omega_2, \omega_1)\rangle = \tilde{\mu}_j|\phi_i^{(1)}(\omega_1)\rangle \qquad (5)$$

where H_0 is the unperturbed Hamiltonian, $|g\rangle$ is the ground state wave function, E_0 is the ground state energy, $|\phi_i^{(1)}(\omega_1)\rangle$ and $|\phi_{ji}^{(2)}(\omega_2, \omega_1)\rangle$ are the first and second order correction vectors and $\tilde{\mu}_i$ is the dipole displacement operator defined as $\tilde{\mu} = (\vec{\mu} - \mu_g)$.

$|\phi_i^{(1)}(\omega_1)\rangle$ and $|\phi_{ij}^{(2)}(\omega_1, \omega_2)\rangle$ are expanded in terms of the eigenvectors of the $\hat{H}_0$ as

$$|\phi_i^{(1)}(\omega_1)\rangle = \sum_n \frac{\langle g|\tilde{\mu}_i|n\rangle}{\hbar(\omega_{ng} + \omega_1)}|n\rangle \qquad (6)$$

$$|\phi_{ij}^{(2)}(\omega_1, \omega_2)\rangle = \sum_m \sum_n \frac{\langle m|\tilde{\mu}_j|n\rangle\langle n|\tilde{\mu}_i|g\rangle}{\hbar^2(\omega_m + \omega_2)(\omega_n + \omega_1)}|n\rangle \qquad (7)$$

where $|g\rangle$ is the ground state wavefunction, $|n\rangle$ and $|m\rangle$ are the excited states of the unperturbed Hamiltonian H_0. The third harmonic generation coefficients can be expressed in terms of correction vectors as

$$\gamma_{ijkl}(-\omega_1 - \omega_2 - \omega_3; \omega_1, \omega_2, \omega_3) =$$
$$\hat{P}_I(\langle\phi_i^{(1)}(-\omega_1 - \omega_2 - \omega_3)|\tilde{\mu}_j|\phi_{kl}^{(2)}(-\omega_1 - \omega_2, -\omega_1)\rangle)$$

Complete active space second-order perturbation theory (CASPT2) calculations are carried out using Molpro 2010 package.[45] CASSCF recovers a part of the static electron correlation which is absent in Hartree-Fock (HF) method. A part of dynamic correlation is recovered by the CASPT2 method using CASSCF as reference wavefunction. CASSCF calculations and CASPT2[46,47] calculations comprise seven occupied pπ orbitals and three unoccupied pπ orbitals and hence 14 electrons are distributed among 10 active orbitals.

3 Results and Discussion

The linear and non-linear optical properties of all the above mentioned system have been calculated using the DMRG method and semi-empirical PPP model Hamiltonian approach. We found that all the systems have a strong optical gap above 1.7 eV except **1** which has an additional low energy weak absorption at 0.84 eV. Charge gap of these conjugated systems, defined as

$$E_c(N) = E^+(N) + E^-(N) - 2E_{gs}^0(N) \qquad (8)$$

is large and comparable to the usual conjugated systems[48] where E^0, E^+ and E^- are the energies of neutral, cation and anion species, respectively. The singlet-triplet gap is large for all the systems except for **1**; the small value of **1** (0.14 eV) is in good agreement with its experimental value (0.18 eV).[34] Experimentally, **1** has a weak absorption at 0.73 eV and a strong absorption at 1.94 eV.[49] **2-4** have their absorptions at 1.70 eV,[49] 2.24 eV,[50] and 1.60 eV,[51] respectively. The results are listed in Table 1, showing a good agreement between theory and experiment. Even though the optical gaps calculated by the DFT method is in good agreement for **1**, the optical gaps for **2** and **4** are overestimated. The MP2 method overestimates the optical gap for all the molecules in the present study. The singlet-triplet gap calculated by the CASPT2 method is in good agreement with those calculated by the DMRG method.

Table 1 Optical gap, charge gap, and singlet-triplet gap (in eV) of diradical systems considered in this study. Experimentally observed optical gaps are shown in the second column. Third, fourth, fifth, and sixth column gives the optical gap calculated with DFT:UB3LYP/6-311G*, TDHF//MP2/6-311G*, CASPT2, and semi-empirical PPP model Hamiltonian using DMRG method, respectively. μ_{ge} is the transition dipole moment (in Debye) calculated between ground and excited state. Experimentally observed singlet-triplet gap of **1** is 0.18 eV.

| system | optical gap | | | | | singlet-triplet gap | | charge gap |
	expt.	DFT	MP2	CASPT2	DMRG (μ_{ge})	DMRG	CASPT2	DMRG
1	0.73	0.79	1.29	1.20	0.84 (1.47)	0.14	0.16	4.79
	1.94	2.05	2.39	2.41	1.99 (3.55)			
2	1.70	2.35	2.53	2.69	2.00 (2.46)	0.81	0.63	5.72
3	2.24	2.49	3.14	2.77	2.67 (5.90)	0.86	0.84	5.75
4	1.60	2.89	2.58	2.71	1.79 (1.87)	0.68	0.72	5.75

But the optical gaps calculated by CASPT2 are overestimated, similarly to the MP2 values.

Usually, conjugation length of the system should be large to get a low energy absorption. But the system with 20 π-electrons gives a very low energy absorption, which is surprising. For a fully conjugated system, the highest occupied natural orbital (HONO) will be doubly occupied, while the lowest unoccupied natural orbital (LUNO) will be empty, while for a pure diradical system, HONO and LUNO will have the occupation number equal to one. Deviation from double occupancy of HONO is considered as the criteria for diradical character.[52] The natural orbital occupation numbers are calculated as explained in the introduction for all the above molecules and plotted in Fig. 3.
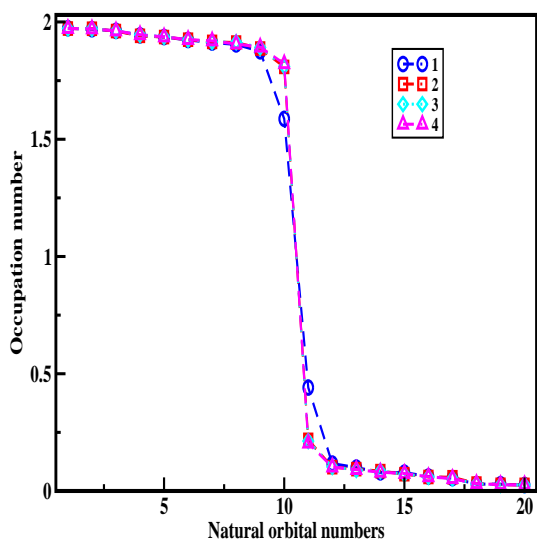
Fig. 3 Natural occupation numbers of all the molecules using ab initio DMRG. The lines are guides for the eye to show the natural occupation numbers.

We see from Fig. 3 that **1** is more diradical in nature, since its HONO (LUNO) occupation number substantially differs from two (zero). Still **1** is not pure diradical. **2**-**4** have small diradical character, while **1** has intermediate diradical character. We also calculated the Head-Gordon's index,[53–55]

$$n_{HG} = \sum_i min(n_i, 2 - n_i) \tag{9}$$

where n_i is the occupation number of ith molecular orbital whose maximum is 2 and minimum is zero, to quantify "effective unpaired" electrons in the system, and it is shown in Fig. 2. This index also confirms that **1** is more diradical, and all its isomers have similar diradical character. Diradical character (y) is also calculated as[56]

$$y = 1 - 2T/(1 + T^2) \tag{10}$$

and T is calculated using occupation numbers of unrestricted HF method as

$$T = (n_{HONO} - n_{LUNO})/2. \tag{11}$$

This also confirms that **1** has intermediate diradical character while all its isomers have very small diradical character.

Table 2 Head-Gordon index (n_{HG}) calculated using Eq. 9 and diradical character using Eq. 10.

system	1	2	3	4
n_{HG}	2.03	1.54	1.52	1.50
y	0.14	0.03	0.03	0.02

Its response to optical gap for all the systems is shown in Table 3. With increase in the site energies, there is a red shift in the optical gaps for **2**, **3**, and **4** but a blue shift in the optical gap for **1**. It is shown that we can tune the optical gaps of the above molecules by proper substitution and can be used as a donor material for photovoltaic applications. Singlet-triplet gap increases for **1** and **3**, while decreases for **2** and **4** with the increase in the site energies.

Table 3 Optical gap and singlet-triplet gap (in eV) of diradical systems considered in this study as a function of site energy (in eV). $\varepsilon_i = \varepsilon$ at positions s and s' denoted in Figure 1, $\varepsilon_i = 0$ for all other positions.

system	ε	optical gap	singlet-triplet gap
1			
	0	0.84	0.14
	2	1.22	0.27
	3	1.36	0.36
	4	1.47	0.47
2			
	0	2.00	0.81
	2	1.89	0.67
	3	1.70	0.59
	4	1.47	0.49
3			
	0	2.67	0.86
	2	2.67	0.89
	3	2.55	0.93
	4	2.40	0.97
4			
	0	1.79	0.68
	2	1.78	0.62
	3	1.65	0.58
	4	1.47	0.52

Table 4 Calculated γ_{xxxx} and γ_{av} of diradical systems at $\omega = 0.65$ eV for **1-4** using the correction vector method as as a function of site energy (in eV). $\varepsilon_i = \varepsilon$ at positions s and s' denoted in Figure 1, $\varepsilon_i = 0$ for all other positions.

system	ε	γ_{xxxx} (a.u.)	$\overline{\gamma}_{av}$ (a.u.)
1			
	0	32.7×10^6	66.4×10^5
	2	9.1×10^6	24.0×10^5
	3	-0.1×10^6	-5.6×10^5
	4	-26.1×10^6	-65.7×10^5
2			
	0	4.0×10^6	8.2×10^5
	2	2.0×10^6	43.2×10^5
	3	-3.8×10^6	-14.0×10^5
	4	-3.7×10^6	-13.4×10^5
3			
	0	3.6×10^6	7.8×10^5
	2	4.1×10^6	8.7×10^5
	3	4.2×10^6	9.0×10^5
	4	3.3×10^6	7.8×10^5
4			
	0	-4.4×10^6	-1.0×10^5
	2	-5.9×10^6	-16.3×10^5
	3	-3.2×10^6	-9.9×10^5
	4	-3.4×10^6	-14.3×10^5

As we discussed in the introduction, systems with intermediate diradical character will have large second order hyperpolarizability (γ) which would have a higher value for **1**. In order to validate this, we calculated the second order hyperpolarizability of all the above systems at 0.65 eV, away from resonance for all the molecules, using the CV method.

The tumbling averaged NLO coefficients $\overline{\gamma}_{av}$ are defined as tensors averaged over all molecular orientations. These are useful quantities to compute, when we need to compare theoretical values with experiment carried out in liquid phase or gas phase. Simple averaging of the tensors leads to the following expressions

$$\overline{\gamma}_{av} = (1/15) \sum_{i=1}^{3} \sum_{j=1}^{3} (2\gamma_{iijj} + \gamma_{ijji}) \quad (12)$$

All the molecules are aligned along the x-axis and the value of γ_{xxxx} is the largest in molecule **1**, compared to **2-4** as seen in Fig. 4 along with $\overline{\gamma}_{av}$.

The third harmonic generation coefficient is the largest for molecule **1**, which has intermediate diradical character, whereas **2**, **3** and **4** have an order of magnitude smaller, while it is negative for **4**. The effect of substitution (change in the site energy) will produce a large difference in the dipole moment and optical gap between the ground and excited states

of the molecule, which eventually changes γ value. The THG coefficient of **1**, **2**, **3** and **4** changes with the site energies and are given in the Table 4. For **1** and **2**, the THG coefficient (γ_{xxxx}) changes its sign with increase in the site energies, still the magnitude of γ_{xxxx} is largest for **1**.

4 Conclusions

We studied linear and nonlinear optical properties of systems with 20 π electrons. It is found that molecule **1** shows small singlet-triplet gap and small optical gap compared to **2-4**, in accordance with experimental observation. Optical gaps calculated by DMRG method correlate well with experimental values better than those calculated by DFT, MP2, and CASPT2 methods. The ab initio DMRG method is used to calculate the natural orbital occupation number to find the HONO and LUNO and it is found that molecule **1** has intermediate diradical character. Third harmonic generation coefficient calculated using correction method and DMRG method is correlated with its diradical character. Molecules **2-4** each has small singlet-triplet gap and their optical gap is more than twice of the singlet-triplet gap. These molecules have optical gap around 2 eV where solar flux is the maximum. By proper substitution, these molecules can serve as good donor materi-

als for photovoltaic applications.

5 Acknowledgments

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