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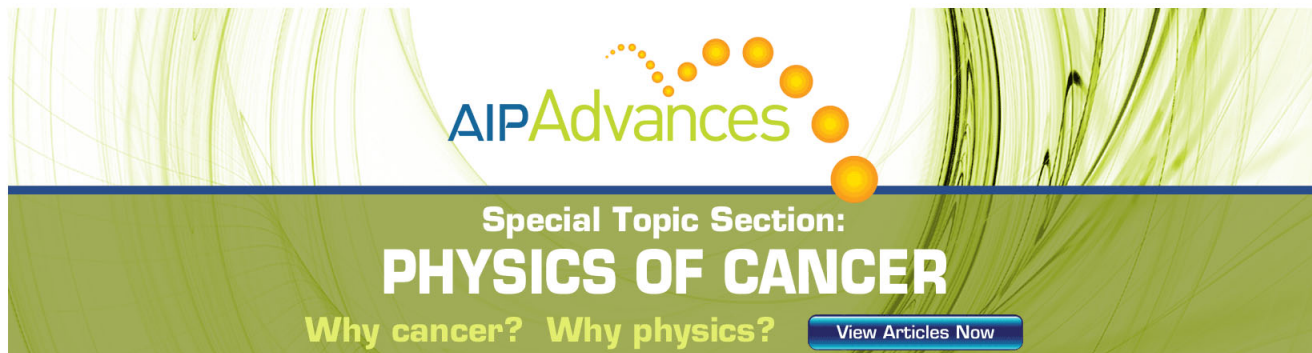
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Variational-perturbational treatment for the polarizabilities of conjugated chains. II. Hyperpolarizabilities of polyenic chains

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We use a perturbative density matrix treatment to investigate the behavior of the first and second static hyperpolarizabilities of linear conjugated chains C_NH_{N+2} described by a Pariser-Parr-Pople Hamiltonian. We examine the evolution of the hyperpolarizabilities with increasing chain lengths, and the effect of different conformations (such as those corresponding to soliton and polaron defects) and of different charge states on the polarizability response of the chains. It is shown that charged soliton chains have large first hyperpolarizabilities β , and that the behavior of the different components of the second hyperpolarizability tensor γ_{iiii} is highly dependent on the geometry and charge of the conjugated chain. In all cases, the contribution of the longitudinal component is shown to dominate the orientationally averaged hyperpolarizability of the chains.

I. INTRODUCTION

In the previous paper¹ (hereafter referred to as I), we have introduced a variational-perturbational treatment for the calculation of linear and nonlinear static polarizabilities of organic molecules. For large conjugated molecules, the polarization response to an external electric field of strength F will be dominated by the π electrons; as is well known, in linear chains the π polarizabilities increase nonlinearly with the size of the molecule.² In I we have shown that the linear polarizabilities of polyenic chains C_NH_{N+2} depend on the conformation and charge state of the system; e.g., the way that the longitudinal component α_{xx} scales with the number of carbon atoms in the chain varies from $N^{1.8}$ in regular polyenes to $N^{2.6}$ in singly charged polarons.

Recently, the effect of conformational changes on the optical properties of solutions of conjugated polymers became a point of interest as a consequence of the observation of remarkable color changes of polydiacetylene solutions upon variations on temperature or concentration of a non-solvent³ and of the fact that these changes have been associated to conformational transitions in individual polymer chains.⁴ In a previous letter,⁵ we have presented preliminary results for the longitudinal second hyperpolarizability γ_{xxxx} of polyenic chains and have shown that, at least for short chains, conformational defects, if present, would dominate the polarization response of the system. More surprisingly, we have found that the charge state of the defect could even affect the sign of γ_{xxxx} . For instance, while singly charged polarons have negative second hyperpolarizabilities which scales as the 6.6 power of N , γ_{xxxx} is positive and evolves as the 6.0 power of N for doubly charged polarons (bipolarons).

The measured second hyperpolarizability for polymers in solution or gas phase is an orientational average of the $xxxx$, $xyyy$, and $yyyy$ components.^{6,7} While for soliton chains

(which belong to the C_{2v} group), only those three components of γ exist, for regular polyenes and polaron chains (C_{2h} group) there are five independent components of the second hyperpolarizability tensor to be determined. On the other hand, the first hyperpolarizability tensor β_{ijk} , which vanishes for systems with inversion symmetry, can be in principle different from zero for soliton-bearing chains.

Previous experimental and theoretical work on the nonlinear optical response of conjugated systems has been usually devoted to the investigation of the second hyperpolarizability γ . In I, we reviewed the corresponding theoretical calculations of γ for polyenes. Here, we will just point out that in calculating the nonlinear polarizabilities of conjugated systems, one is forced to attain a compromise between the level of approximations introduced in the Hamiltonian and the size of the molecules to be examined; to our knowledge, self-consistent treatments including the σ backbone have only been implemented for $N \leq 8$ polyenes,⁸ while previous usage of the PPP approximation was limited to small polyenes in the regular (i.e., with no defects present) conformation⁹ or $N \leq 14$ molecules with homogeneous bond length along the chain.¹⁰ The only experimental data available for the hyperpolarizabilities of polyenes was obtained by Ward and Elliott who have used a dc electric-field-induced second-harmonic generation technique to measure the effective γ of small conjugated molecules in vapor phase.¹¹ They have unambiguously determined the sign of γ to be positive for 1,3-butadiene and 1,3,5-hexatriene. The butadiene sample used was essentially in the *trans* form, with a small ($< 1\%$) presence of the *cis* isomer, while for hexatriene a mixture of poorly known concentrations of *cis* (10%–40%) and *trans* (90%–60%) isomers was used. No experimental results for the polyacetylene ($N \rightarrow \infty$) polymer are available.

In this paper, we present results for the first and second hyperpolarizabilities of polyenic chains. We show that although the first hyperpolarizabilities β of neutral soliton chains are exceedingly small, some of the β components can be quite large for charged solitons. For the negatively charged soliton chain (S^-) with $N = 21$, e.g., the predicted

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value for the xyy component of β is 1.79×10^6 a.u.; for this family of molecules, β_{xyy} scales roughly as N^3 . We also compute the orientationally averaged second hyperpolarizabilities γ^π of regular polyene, soliton and polaron chains; the sensitivity of the γ^π 's to the conformation and charge state of the conjugated chain is much more pronounced than that of the corresponding average linear polarizabilities, similar to the behavior found when the longitudinal components of α and γ are compared.

II. CALCULATION

We have adopted the same Hamiltonian and model geometries as those utilized in I. The molecules are assumed to be oriented along the x axis. The PPP Hamiltonian only considers explicitly the π electrons; in spite of this, it is well-known to lead to reasonably good results for the electronic structure of conjugated molecules¹². By the semiempirical nature of the PPP Hamiltonian, however, one should not expect the corresponding results to be quantitatively reliable, but rather that trends and patterns could emerge as the nonlinear optical response of conjugated systems is examined for different charge states and chain conformations. One should also note that even if the σ -electron contribution is known to evolve only linearly with the chain size, its importance cannot be ruled out *a priori*, specially for the small N molecules.

Through the perturbative expansion for the density matrix (PEDM) procedure, it is possible to obtain expressions for the successive orders of the polarization response, which are independent of the strength of the applied field. As shown in I, once the first-order correction for the density matrix R^1 is determined, the linear polarizability α and the first hyperpolarizability β can be calculated. On the other hand, to determine γ we have to solve a self-consistent equation involving the second-order density matrix correction R^2 .

We have found that both iterative equations for R^1 and R^2 can be most efficiently solved in the basis in which the unperturbed density matrix R_0 is diagonal; we were then able to satisfy both in first and second orders the idempotency of the density matrix and its commutation relation with the Hamiltonian to at least 10^{-5} for all molecules considered.

The rotationally averaged first and second hyperpolarizabilities are given, respectively, by^{6,7}

$$\beta^\pi = \beta_{xxx} + \beta_{xyy} \quad (2.1)$$

and

$$\gamma^\pi = 1/5(\gamma_{xxxx} + 2\gamma_{xxyy} + \gamma_{yyyy}), \quad (2.2)$$

since the molecules are considered to be planar.

III. RESULTS

A. First hyperpolarizabilities

By symmetry, the first hyperpolarizability tensor β_{ijk} vanishes for regular polyenes and polaron chains. For molecules belonging to the C_{2v} group, in principle three independent nonzero components (β_{xxx} , β_{xxy} , and β_{yyy}) can exist; we have found, however, that for neutral soliton chains all

components of the first hyperpolarizability tensor are negligible.

For charged solitons, on the other hand, while β_{xxx} remains exceedingly small, the magnitudes of the other two components are large and increase with the size of the chain. β_{xyy} is the largest of them by at least one order of magnitude; for the largest soliton chain examined ($N = 21$), e.g., $\beta_{xyy} \sim 630\beta_{yyy}$. Contrary to what it is observed for linear polarizabilities and second hyperpolarizabilities, the signs (although not the absolute values) of all components of β depend on the ionization state of the molecule, while for the $N = 5, 9, 11, \dots, S^+$ chains, the β 's are increasingly negative, exactly the same absolute values and opposite signs are obtained for the corresponding S^- chains.

The absolute values of β_{xyy} for the soliton chains examined are presented in Fig. 1. No saturation effect with the increasing in size of the chain for the first hyperpolarizabilities can yet be seen for the range of N considered, and the data is well reproduced by a linear regression of the form $16.4 N^{3.05}$. As one can see from expression (2.1), in the present case the orientationally averaged first hyperpolarizability β^π depends solely on this component of β .

B. Second hyperpolarizabilities

For regular polyene and polaron chains, there are five independent components ($xxxx$, $yyyy$, $xxyy$, $xyyy$, and $xxxy$) for the second hyperpolarizability tensor γ . For solitons, only the first three components exist. Therefore, while for chains belonging to the C_{2h} group, the calculation of the fourth-order energy correction {which involves the time-consuming step of achieving the self-consistent solution for the commutation relation for R^2 [cf. Eq. (6) of I]} has to be performed for five different directions of the external field, only three distinct orientations of F suffice for the complete determination of the γ_{ijkl} tensor for soliton chains.

As could be expected from symmetry considerations, the magnitude of γ_{xxxx} turns out to be the largest of all components of γ in each case. However, the results show remarkable dependence on the conformation and charge of the chain. All neutral molecules have positive longitudinal component, whose variation with chain size is represented in Fig.

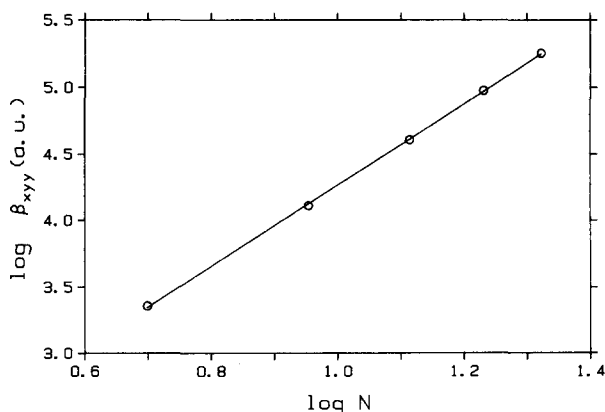


FIG. 1. Evolution of the xyy component of the first hyperpolarizability β of charged soliton chains.

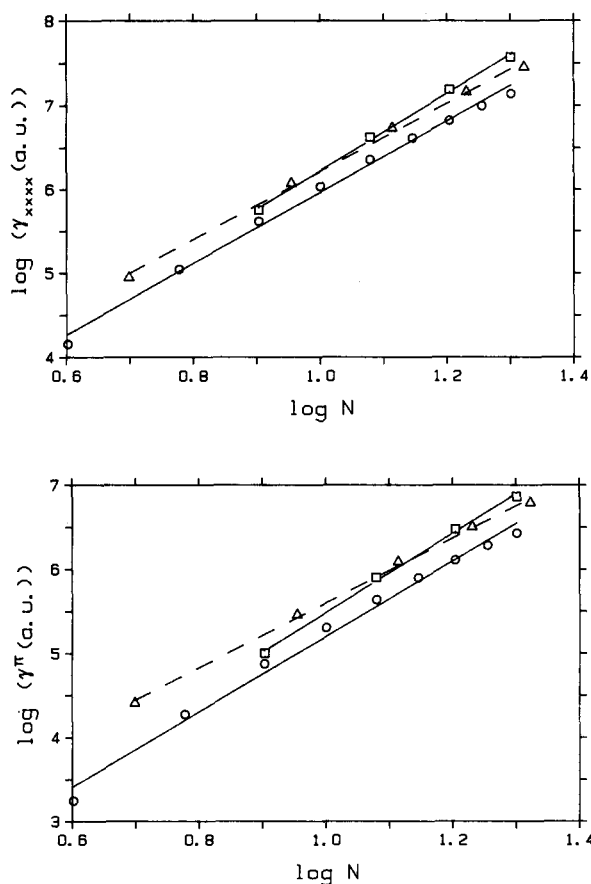


FIG. 2. Second hyperpolarizabilities for chains of regular polyenes (O), neutral soliton (Δ), and neutral polarons (\square). (a) Longitudinal component γ_{xxxx} . (b) Orientational average γ^π .

2(a). While for neutral solitons the $xyyy$ and $yyyy$ components are positive and increase monotonically with N , the γ_{xxxxy} component of regular polyenes and neutral polarons has a peculiar behavior. Initially, it is negative and increases in absolute values as N increases; for larger N , it turns around and becomes positive. All remaining ($xyyy$, $xyyy$, and $yyyy$) components of γ are negative for regular polyenes and neutral polarons and have monotonically increasing magnitudes. The values of the different components of the γ tensor for the largest chains considered in each case are presented in Table I. The fact that γ_{xxxx} dominates the optical response of these systems is shown by the positive values assumed by the orientationally averaged second hyperpolarizability γ^π in all cases; the variation of γ^π with N for neutral chains is represented in Fig. 2(b). The data of Fig. 2 indicates that up to the $N \sim 20$ range the onset of saturation with the chain size does not occur either for the longitudinal component $xxxx$ or for the averaged polarizability γ^π . The corresponding calculated values are reasonably well reproduced [with the possible exception of regular polyenes (see later)] by straight lines; the fitting can be cast under the general form aN^b and the appropriate parameters are presented in Table II.

We have found the longitudinal component γ_{xxxx} to be negative for charged solitons (either S^+ or S^-) and singly charged polarons. This result can be of special significance

TABLE I. (A) Values of the different components of the second hyperpolarizability γ for the largest chains ($N = 20$) of regular polyenes (rp), neutral polarons (np), singly charged polarons (cp), and bipolarons (bp). (B) Values of the different components of the second hyperpolarizability γ for the largest chains ($N = 21$) of neutral (ns) and singly charged (cs) soliton chains.

	rp	np	cp	bp
γ_{xxxx} (10^7 a.u.)	1.379	3.745	-103.0	1.728
γ_{xxxxy} (10^5 a.u.)	3.514	6.503	-172.2	83.26
γ_{xyyy} (10^5 a.u.)	-1.627	-3.993	-239.7	-2.384
γ_{xyyy} (10^3 a.u.)	-6.130	-12.80	-315.1	2.960
γ_{yyyy} (10^3 a.u.)	-17.88	-32.38	-39.47	-4.278
		ns		cs
γ_{xxxx} (10^7 a.u.)		2.858		-5.791
γ_{xyyy} (10^5 a.u.)		11.45		16.11
γ_{yyyy} (10^3 a.u.)		15.01		0.9176

once experimental results for the nonlinear polarizability of doped polyacetylene become available, since it is well known about the important role played by charged conformational defects on the optical and transport properties of the material.¹³ The evolution with chain size of the magnitude of γ_{xxxx} for charged defects is depicted in Fig. 3(a). The $xyyy$ component of γ for charged solitons is monotonically increasing positive, while the $yyyy$ component starts as being negative and then suffers a sudden change of sign becoming increasingly positive for larger chains. For singly charged polarons, all five components are of negative sign and have magnitudes which monotonically increase with N . Finally, for bipolarons, only the $xyyy$ and the $yyyy$ components are negative, but all five of them have absolute values which increase with N . The values of the different components for the largest value of N examined for each of the three charged chains considered are also presented in Table I. As found for the neutral chains, the orientationally averaged hyperpolarizability is dominated by the longitudinal component $xxxx$ and, as a result, the calculated γ^π 's are negative for charged solitons and singly charged polarons. The evolution of γ^π with chain size for charged chains is represented in Fig. 3(b). Once again, the data is well reproduced by a fitting of aN^b form and the corresponding parameters can be found in Table II.

TABLE II. a and b parameters derived from linear least-squares fitting aN^b for calculated values (in a.u.) of the longitudinal component (γ_{xxxx}) and orientational average (γ^π) of the second hyperpolarizability of finite chains of regular polyenes (rp), neutral solitons (ns), neutral polarons (np), charged solitons (cs), singly charged polarons (cp), and bipolarons (bp).

	rp	ns	np	cs	cp	bp	
γ_{xxxx}	a	52.0	146	42.0	-7.0	-2.66	0.247
	b	4.25	4.05	4.60	4.79	6.57	6.04
γ^π	a	5.27	56.4	5.98	-5.16	-1.17	0.045
	b	4.48	3.85	4.71	4.79	6.32	6.07

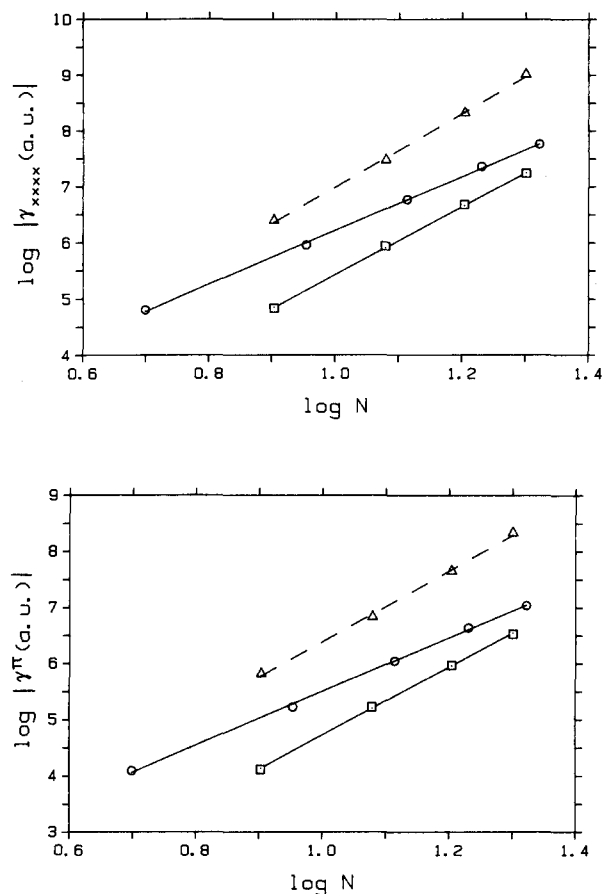


FIG. 3. Second hyperpolarizabilities for charged solitons (O), singly charged polarons (Δ), and bipolarons (\square). (a) Longitudinal component γ_{xxxx} . (b) Orientational average γ^π .

IV. DISCUSSION

The above results indicate that the second hyperpolarizabilities of conjugated chains are extremely sensitive to the conjugation pattern along the chain. This is a confirmation of the behavior first observed for the linear polarizabilities of polyenes.¹ Considering the role that doping by both electron-rich and electrophilic agents plays on the electronic and optical properties of polyacetylene,¹³ it is also important to point out the effect of different ionization states on the optical response of the system. As our results show, for a given conformation of the conjugated chain, the nonlinear response of the system is extremely affected by the presence of charge along the chain.

Although our results are based on a simple semiempirical scheme, we expect that the general trends and patterns here appointed for the effect of conformational and charge transfer upon the polarization response of conjugated systems will be confirmed by more elaborate calculations. For example, in the analysis of the behavior of the first hyperpolarizability β of soliton chains, the fact that exactly the same numerical value with opposite signs are obtained for the β components of S^+ and S^- chains reinforces our belief that symmetry is correctly handled in the calculation.

To our knowledge, the only other calculations which

have examined the evolution of the hyperpolarizabilities of polyenes were performed at the free-electron¹⁴ and simple Hückel levels¹⁵; while the former has predicted that for regular polyenes γ_{xxxx} would scale as the fifth power of N , the Hückel treatments gives a value of b equal to 5.257. Since previous calculations were usually performed for the regular conformation of the polyenic chain, no results for the first hyperpolarizability β are available.

Papadopoulos *et al.* have applied a PEDM treatment similar to ours and based on the CNDO approximation to compute the second hyperpolarizabilities of small polyenes.⁸ They have optimized the orbital exponents in their basis set to reproduce the experimental values of γ^π for both ethylene and hexatriene, as obtained by Ward and Elliott.¹¹ In Table III, our results for the regular chains are compared to the available theoretical and experimental data. For small polyenes, Zamani-Khamiri and Hameka¹⁶ have included the σ -electron contribution through an independent extended Hückel calculation. From what we have learned here about the effect of conformational changes upon the polarization response of conjugated chains, one can understand the reason for the large values predicted by the valence perturbation PPP treatment of Zamani-Khamiri and Hameka¹⁰ for the second hyperpolarizability of the polyenes. In their calculation, a nonbond-alternating geometric structure for the polyenic chain was adopted, thus exacerbating the conjugation character of the system. As shown by Bodart *et al.*,¹⁷ the linear polarization response of polyenes increases with the degree of delocalization along the conjugated chain, and the above results indicate that this sensitivity to conformational changes should be even greater for the nonlinear optical response. By the same token, the experimental results obtained for butadiene, and specially hexatriene, should be analyzed under the caveat that the samples used were poorly defined mixtures of *cis* and *trans* isomers.

One can see from Table III that the difference between our results and those of Papadopoulos *et al.* is larger for the *trans*-butadiene molecule. Besides the fact that we have not introduced any specific parameter optimization procedure, one possible reason for that difference is that in our treatment the polarization response of small molecules was un-

TABLE III. Orientationally averaged hyperpolarizability γ^π for regular polyenes C_NH_{N+2} (in a.u.).

N	This work	Other calculations	Experiment
4	1 759	16 021 (PPP + H) ^a 33 447 (PEDM-CNDO) ^b	27 397 \pm 1549
6	18 812	118 166 (PPP + H) ^a 72 137 (PEDM-CNDO) ^b	89 696 \pm 8338
8	75 007	817 272 (VPT-PPP) ^c 124 313 (PEDM-CNDO) ^b	...
10	202 739	2 209 693 (VPT-PPP) ^c	...
12	433 828	4 929 911 (VPT-PPP) ^c	...
14	791 689	9 237 925 (VPT-PPP) ^c	...

^a Reference 16.

^b Reference 8.

^c Values of Ref. 6 multiplied by a factor of 6 to take in account difference in coefficients in the expansion of the energy as a function of field strength.

derestimated by the neglect of the σ -electron contribution. In fact, the corresponding values of both γ_{xxxx} and γ'' do not lie close to the straight line fits of Fig. 2. We have verified, however, that even if the $N = 4$ data points are excluded, a linear regression analysis gives values of b equal to 4.00 and 3.93 for γ_{xxxx} and γ'' , respectively. Thus, the basic qualitative trend is not altered by the exclusion of the butadiene data. Finally, we observe that the calculated values (including the $N = 4$ case) are smoothly fitted by fourth-order polynomial expressions and, as a consequence, the behavior of the hyperpolarizabilities per unit cell do not reveal any indication of saturation up to the value of N examined.

V. CONCLUSION

The present calculation leads to specific predictions for the qualitative behavior of the nonlinear static polarization response of conjugated chains, such as a remarkable difference in the evolution of the second hyperpolarizability for neutral and charged chains of same geometry, and the extreme sensitivity of that response to conformational changes. It is also pointed out that, as opposed to what is found for neutral solitons, the first hyperpolarizability of charged solitons can be large and should increase with the length of the chain. Finally, even for chains of regular geometry, the hyperpolarizabilities are expected to attain saturation with the increase of N at a much larger range than what was predicted for the linear polarizabilities.¹

These results, of course, need to be verified by more elaborate calculations and by experimental measurements. We note, however, that conflicting results for the sign of the second hyperpolarizability of polydiacetylene samples¹⁸⁻¹⁹ could be reconciled if similar dependence on conformational changes occur for the polarization response of those conjugated molecules. We are at present applying the PEDM

technique to investigate the polarizabilities of polydiacetylene chains.

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