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Electronic Properties of Polymethine Systems. Part 4: Electronic Structure of Polymethine Chain

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ABSTRACT

On the basis of the topological concept of electron donor ability, the electronic structure is considered for two main classes of symmetric linear polymethine systems, polymethine dyes and hetarylpolyenes. Quantum-chemical evidence and analytical relations are presented which account for substantial distinctions between polymethines and polyenes in the π*-electronic density distribution over atoms and bonds, both in the ground and excited states. Existence conditions for so-called ideal polymethinic and polyenic states are expressed in terms of electron donor abilities defined for end-groups, and for a polymethine system as a whole.*

1 INTRODUCTION

Previous papers in this series[1–3] treated linear polymethine systems (LPMS) I in terms of their frontier level positions, relative molecular redox stability, and the nature of the electronic transitions, taking into account both their classification into two types, viz., polymethines and polyenes, and the topology of their end groups (EG).

$$\overset{\cdots\cdots\cdots\cdots\cdots\cdots}{G_1 - (CH)_m - G_2}$$

I

Symmetric polymethine dyes (PMD) ($G_1 = G_2$, $m = 2n + 1$) containing N π-centres in the molecule were shown to exist, as a rule, in a single stable

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form which is either an electron-excessive one with $N + 1$ electrons or an electron-deficient one with $N - 1$ electrons. For unsubstituted polymethines ($m = N$) or PMD containing alternant hydrocarbons as EG, both these forms are possible, but are, however, rather unstable.

On the contrary, the electron-excessive (containing $N + 2$ electrons) and electron-deficient (containing $N - 2$ electrons) forms are quite stable for disubstituted hetarylpolyenes (HP) ($m = 2n$) and as regards unsubstituted polyenes ($m = N$), there is in addition an electron-balanced form (N electrons).

The positions of the highest occupied and the lowest unoccupied molecular orbitals (HOMO and LUMO, respectively) with energies e_g and e_e can be specified with respect to the Fermi level by the electron donor ability of a LPMS molecule, φ_0:[1]

$$\varphi_0 = 90^\circ \frac{\varepsilon_e - \alpha}{\varepsilon_e - \varepsilon_g} \tag{1}$$

At the same time, the electron level positions and the nature of the first electronic transition proved to depend significantly on the EG topology that is conveniently represented by the indices Φ_0 and L.[1,4–7] The former is simply related to the molecular electron donor ability by eqns (2) and (3):

$$\Phi_0 = \lim_{m\to\infty} \varphi_0 \qquad \text{(polymethines)} \tag{2}$$

$$\Phi_0 = \lim_{m\to\infty} \varphi_0 \pm 45^\circ \qquad \text{(polyenes)} \tag{3}$$

(The sign in eqn (3) is determined by the HP form).

It is our intention in this present paper to follow the ground- and excited-state electronic density distribution over atoms and bonds of the polymethine chain (PC) in symmetric LPMS depending on the EG topological index Φ_0; relations of this type are of value for correctly interpreting electronic transitions in polymethine compounds.

Neglecting differential overlapping, electronic populations are calculated from the molecular orbital coefficients, $C_{i\mu}$:[8]

$$q_\mu = \sum_i n_i C_{i\mu}^2; \qquad p_{\mu\nu} = \sum_i n_i C_{i\mu} C_{i\nu} \tag{4}$$

where n_i is the ith MO occupation, q_μ is the electron density on the μth atom, and $p_{\mu\nu}$ is the bond order for the μth and νth atoms (hereinafter, with the exception of eqns (8) and (9), atoms are numbered from the PC ends).

To study EG effects on the molecular electronic properties, EG will be simulated by heteroatoms of variable electronegativity, X, so that G = —CH$\overset{\cdots}{=}$$X$. Then, in the framework of the Hückel model, the topological index Φ_0 is determined as tg $\Phi_0 = \eta^2/h$, where h and η are the Coulomb and resonance integrals of the heteroatom X and the bond CX (expressed in the units of the CC bond resonance integral and reckoned from the Fermi level, or the C-atom Coulomb integral).

2 ELECTRONIC CHARGES ON ATOMS

Ground state

For the electron-balanced form, or N-form, of unsubstituted polyenes, the electron density on the atoms is equalized within the PC: $q_\mu = 1$, i.e. all the PC atoms are uncharged.

For unsubstituted polymethines, the atoms carry no charges provided that the number of π-electrons and π-centres is the same as in the case of the N-form of polymethine radicals. Correspondingly, both closed-shell forms of unsubstituted polymethines imply charged molecules. Since the charge values are equal to the squared atomic coefficients of the non-bonding MO (NBMO), the even atoms on which the NBMO nodes fall are free of charge, whereas odd atoms carry charges, the values of which depend on the PC length (as is evident from a normalization condition):

$$Z = \pm\, 1/(N + 1) \tag{5}$$

Here plus and minus correspond to the electron-deficient ($N - 1$) form or the electron-excessive ($N + 1$) form, respectively.

Introduction of EGs results in a shift of frontier MO nodes which is proportional to the topological index Φ_0, and thus to the electronic density redistribution.

In the Hückel approximation, it is reasonable to simulate the variation of the index Φ_0 by the variable Coulomb integral of the model terminal heteroatom. If the value h is changed slightly, the π-electron density can be estimated using perturbation theory, viz:[9]

$$q_\mu = q_\mu^0 + \pi_{1,\mu} h; \quad \pi_{1,\mu} = \frac{1}{N+1}\left[\frac{2}{\pi} + (-1)^\mu\right] \quad \text{if } \mu \sim \frac{N}{2} \text{ or } \frac{N+1}{2} \tag{6}$$

where q_μ^0 is the electron density on the μth atom of the unsubstituted PC ($X = CH_2$) and $\pi_{1,\mu}$ is the corresponding atom–atom polarizability.

As is evident from eqns (5) and (6), an increase in the electronegativity of the heteroatom X compared to carbon ($h > 0$) makes the π-electron density of the stable electron-excessive ($N + 1$) form shift to EG, causing a decrease of negative charges in odd PC positions, and the induction of positive charges in even PC positions. If the heteroatom X is less electronegative than carbon ($h < 0$) then the electron density of the stable electron-deficient

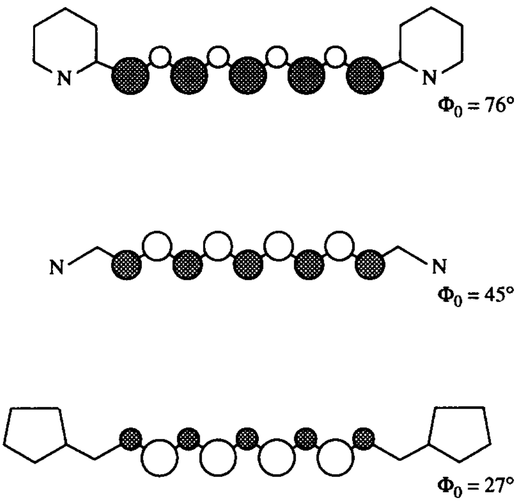

Fig. 1. Ground-state π-atomic charges within the PC of PMD (in the Hückel approximation); ○, positive charge; ●, negative charge.

$(N - 1)$ form is withdrawn to the PC, which corresponds to a decrease of positive charges in odd PC positions and a generation of negative charges in even positions.

For symmetric polymethines, both EG act in accord with each other, as the parities of atom positions are the same irrespective of which PC end they are reckoned from.

With an increasing absolute value of h, odd-position charges drop, while the even-position charges increase. Numerous calculations by the Hückel, PPP, CNDO/2, and MINDO/3 methods[7,10] have shown that the charge magnitude ratio for neighbouring PC atoms depends unambiguously on the topological index Φ_0; positive charges exceed negative ones in the middle of the chain of low-electron-donor PMD (Φ_0, $\varphi_0 < 45°$), whereas the opposite effect is observed for PMD of high electron donor ability (Φ_0, $\varphi_0 > 45°$). In the case of middle-electron-donor polymethines (Φ_0, $\varphi_0 = 45°$), the charges on neighbouring atoms are equal in magnitude. The three instances in question are illustrated in Fig. 1.

Unlike polymethines, the homogeneous distribution of π-electron density over PC atoms and the absence of charges are typical of the stable N-form of unsubstituted polyenes. On changing the electronegativity of one end-atom, alternating positive and negative charges are induced in the PC. Thus, a single EG causes the same effect both for polymethines and polyenes; it generates an electronic density wave shifting to or from EG depending on whether the X-atom electronegativity is greater or smaller than that of a carbon atom.

TABLE 1

Electron Densities, q_μ, on Carbon Atoms of the PC of Polyenes **I** at $m = 6$ Calculated by the CNDO/2 Method with Geometry Optimization

Polyene form	*X*	Φ_0	q_μ		
			$\mu = 1$	$\mu = 2$	$\mu = 3$
$(N - 2)$	$—CH—CH_2$	0°	3·686	4·011	3·790
	$—C{=}N$	63°	3·725	3·983	3·850
	$—CH—O$	76°	3·986	3·854	3·995
N	$—CH—CH_2$[a]	0°	3·988	3·990	3·991
	$—C{=}N$	63°	3·995	3·965	3·985
	$—CH—O$	76°	4·040	3·947	3·985
$(N + 2)$	$—CH—CH_2$	0°	4·263	3·966	4·119
	$—CH—O$	76°	4·248	3·962	4·090

[a] For neutral unsubstituted polyenes, negligible charges arise from the C—H bond polarization.

However, due to the factor $(-1)^\mu$ in eqn (6), the resultant action of two identical EG differs radically in polymethines and polyenes. For the former, parities of atom positions are the same relative to either EG, which is not the case for the latter. As a consequence, two EG in a PMD give rise to the charge alternation in accord with each other, whereas in a HP their effects are mutually compensated, making the sign-variable summands in eqn (6) vanish. Thus, there is no charge alternation in the middle of PC of symmetric HP, and the charge sign is governed only by the sign of the parameter h and the polyene form.

According to quantum chemical calculations, with lengthening of the PC, charge magnitudes on its ends asymptotically tend to certain limiting values which are determined by the topological index Φ_0 and LPMS type; self-consistency procedures make this regularity more evident.[7,10]

On going from one polyenic form to another, the HOMO number changes by 1 and its nodes shift to the neighbouring bonds; as a result, EG effect on the electronic density distribution is reversed. It is notable, in particular, that longer and shorter bonds interchange.[2]

Table 1 presents the caculated electronic densities on C atoms within a six-methine chain for various forms of model polyenes **I**.[11] As can be seen, the electron density alternation is typical of all three forms, being most pronounced for the charged forms which contain $(N + 2)$ or $(N - 2)$ electrons. The alternation amplitude regularly decreases with distance from the chain ends. Also, the electronic density distribution for every form is shown to depend on the nature of EG.

The ground-state alternation of the electron density on PC atoms which is more pronounced in PMD than in HP is consistent with the alternating chemical shifts observed in NMR spectra. To exemplify, both in the case of cationic PMD and oxonols, the ^{13}C chemical shifts differ significantly for neighbouring PC positions: positively and negatively charged atoms exhibit signals at 150–170 and 90–120 ppm, respectively.[12–17] With respect to polyenes, the difference between ^{13}C chemical shifts for neighbouring atoms is no more than 1–2 ppm while the signals are observed in the vicinity of 130 ppm.[18,19]

Excited state

π-Electron densities on atoms in the first excited state, q^*_μ, are conveniently represented as:

$$q^*_\mu = q^0_\mu + \Delta q_\mu; \qquad \Delta q_\mu = C^2_{e\mu} - C^2_{g\mu} \tag{7}$$

with q^0_μ and Δq_μ designating the ground-state electron densities and their changes on excitation.

In the framework of the long-chain approximation developed previously for LPMS,[4–7] the excitation-induced electron density redistribution is expressible by eqns (8) and (9):

$$\text{PMD: } \Delta q_\nu = a(-1)^{n+\nu+1} \cos\left[\nu a \frac{\pi}{2}\right] \cos\left[\nu a\left(\frac{\pi}{2} - 2\Phi_0\right)\right] \tag{8}$$

$$\text{HP: } \Delta q_\nu = a(-1)^{n+\nu} \sin\left[\nu a \frac{\pi}{2}\right] \cos\left[\nu a\left(\frac{\pi}{2} - 2\Phi_0\right)\right] \tag{9}$$

in which $a = 1/(L + n)$ and ν denotes the atomic numbers determined, for convenience, from the middle of the PC, so that $\nu = 0$ for a meso-position.

The factor $(-1)^\nu$ appearing in both equations implies the opposite excitation effects for neighbouring atoms or bonds. This regularity is well illustrated by the PPP-calculated ground- and excited-state electronic densities for PMD and HP (see Fig. 2). At the same time, eqns (8) and (9) differ by trigonometric factors, which gives rise to the essential distinction in the electron density redistribution which occurs on excitation in polymethine and polyene molecules. At a constant PC length, changes in atomic electron densities in the middle of the chain are greater for PMD than for HP. Though the ground-state electron densities on the central PC atoms are much the same for PMD and HP, being inversely proportional to the number of vinylene groups in the chain, the excitation causes these quantities to change in a quite different manner for the two LPMS classes, viz in PMD molecules, atoms in the PC middle undergo a recharge, or a change in charge signs (see Fig. 2a), which is not the case for HP (see Fig. 2b).

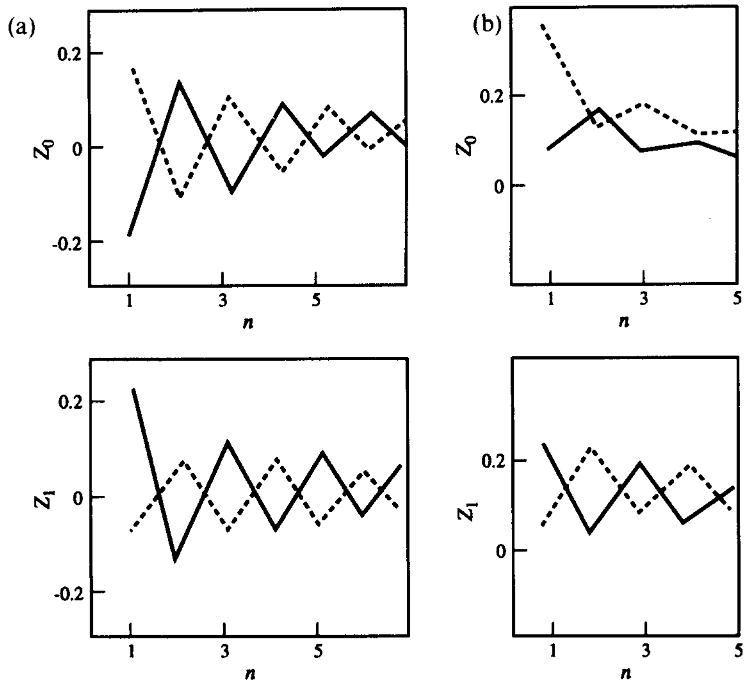

Fig. 2. π-Charges on meso-atom (Z_0) and on neighbouring atoms (Z_1) in the ground (solid line) and excited (dashed line) states of (a) PMD and (b) HP (in the PPP approximation).

On the PC ends, both ground- and excited-state electron density distributions are governed mainly by EG. Since, in accordance with eqn (8), the values Δq_ν for chain-end atoms ($\nu \sim n$) of PMD grow smaller compared to the chain centre, these atoms can retain their charge signs constant on excitation, in contrast to the central atoms.[7,10]

With regard to HP molecules, the electron density redistribution within their PC is about the same, irrespective of the chain region; thus the charge signs are unchanged on excitation both for the end and central atoms.

3 BOND ORDERS

Polymethines

Whereas electron densities on the PC atoms, q_μ, show a pronounced alternation in polymethines and an equalized distribution in polyenes, bond electronic populations, $p_{\mu\nu}$, behave quite oppositely.[1-5] For instance, middle-electron-donor PMD with Φ_0, φ_0 = 45° are characterized by equal bond orders within the PC. As the parameters Φ_0 and φ_0 deviate from the middle value,

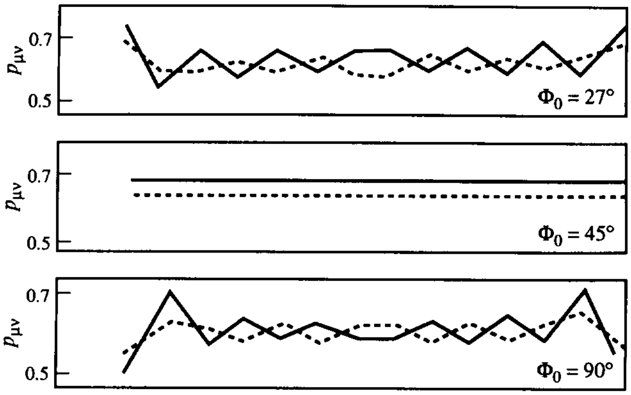

Fig. 3. π-Bond orders within the PC of PMD in the ground (solid line) and excited (dashed line) states (in the Hückel approximation).

calculations show that an enhancing bond-order alternation arises in the PC, the amplitude being minimum in the PC middle and increasing with distance from it[7,21] (see Fig. 3). Not only bond populations, but also the order of alternation of shorter and longer bonds are governed by the EG electron donor ability. In the case of low-electron-donor nuclei ($\Phi_0 < 45°$), the bond order is increased for the first (edge) PC bond, decreased for the second bond, and so forth. The opposite alternation pattern is characteristic of the PC which is bound to the EG of high electron donor ability ($\Phi_0 > 45°$). The absolute values of bond populations are dictated by the magnitude of the Φ_0 deviation from its middle value, 45°. The C—C bond nonuniformity in PMD is confirmed by the roentgenoscopic evidence (see, e.g. Ref. 14) as well as by direct spin–spin coupling constants in NMR spectra.[22,23]

It is apparent from quantum-chemical calculations that bond orders also depend on the bond positions in the PC and the total chromophore length. The values $p_{\mu\nu}$ are less sensitive to EG electron donor ability in the middle of the chain, and with lengthening of it they tend to the limiting value, $2/\pi$.[21]

A bond order difference for two neighbouring bonds, or alternation amplitude $\Delta_\mu = p_{\mu,\mu+1} - p_{\mu+1,\mu+2}$, can serve as a measure of the alternation. As regards relatively long unsubstituted polymethines ($N \gg 1$), this quantity is expressible analytically to a good accuracy by eqn (10):

$$\Delta_\mu = \frac{2(-1)^{\mu+1}}{N+1} \operatorname{ctg} \frac{\pi(\mu+1)}{(N+1)} \tag{10}$$

For the vicinities of PC ends ($\mu = 1, 2, \ldots \ll N$), the following relation holds:

$$\lim_{N\to\infty} \Delta_\mu = \frac{2(-1)^{\mu+1}}{\pi(\mu+1)} \tag{11}$$

whereas in the middle of the long PC ($\mu = (N + 1)/2$), the alternation amplitude decreases, varying in inverse proportion to the squared PC length:

$$\Delta_\mu = \frac{2\pi(-1)^\mu}{(N + 1)^2} \tag{12}$$

Figure 3 shows that the excited-state bond order alternation is much less than that in the ground state, especially for the central PC site. Again, the alternation amplitude increases with the deviation of topological index Φ_0 and electron donor ability φ_0 from the middle value. Interestingly, in the self-consistent-field approximation, bond populations alternate along the whole PC in the same order for the ground and excited states,[7,21] whereas the Hückel method yields the arrangements of shorter and longer bonds for the two states which are similar only near the PC ends and gradually become opposite with increasing distance from them (see Fig. 3).

Polyenes

The alternation amplitude for unsubstituted long polyenes is described by much the same expression as eqn (10), differing only in that the cosecant is involved instead of the cotangent. Near the PC ends, the quantity Δ_μ tends to the same limiting value (see eqn (11)). At the same time, in the middle of the PC, this characteristic is inversely proportional to the chain length, thereby representing an order of magnitude of stronger alternation as compared to polymethines (cf. eqn (12)):

$$\Delta_\mu = \frac{2(-1)^{\mu+1}}{N + 1} \tag{13}$$

A representation of the relationship between the topologic parameter Φ_0 and bond electronic populations within the PC for a number of model HP is given in Fig. 4 (bond orders were obtained by geometry optimization performed as previously reported[11]). As expected from a comparison of eqns (12) and (13), bond order alternation in the middle of the chain is much more pronounced for HP than for PMD (cf. Fig. 3). An essential distinction between these two LPMS types concerns the arrangement of shorter and longer bonds depending on the value Φ_0. While PMD exhibit opposite alternation patterns for $\Phi_0 < 45°$ and $\Phi_0 > 45°$, the value $\Phi_0 = 45°$ is not a boundary one for HP.

As already mentioned, on going from one polyenic form to another, the alternation pattern is reversed (see Fig. 4). On the transition to the first excited state, bond order populations change significantly in HP molecules, viz., the bond orders decrease for essentially double bonds and increase for essentially single bonds as shown in Fig. 4.

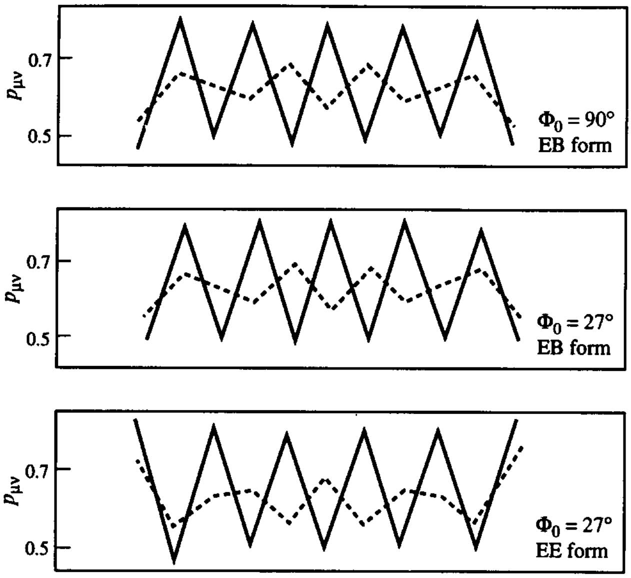

Fig. 4. π-Bond orders within the PC of HP in the ground (solid line) and excited (dashed line) states (in the PPP approximation); EB, electron-balanced form; EE, electron-excessive form.

4 IDEAL ELECTRONIC STATES

As may be inferred from the previous sections, the electronic structure of the PC in symmetric LPMS differs substantially for polymethine and polyene types. Here it is appropriate to invoke the concept of ideal polymethinic and polyenic states introduced previously by Dähne on the basis of his triad theory.[24–26]

The ideal polymethinic state is characterized by the alternation of positive and negative atomic charges, and the equalization of bond orders within the PC. In contrast, the ideal polyenic state implies uncharged atoms, and alternating increased and decreased bond orders.

In the general case of LPMS with arbitrary EG, the conditions for realization of these states are related to the concept of the electron donor ability, φ_0, and EG topological index, Φ_0. Thus, the ideal polymethinic state of PMD occurs when Φ_0, and hence φ_0 (see eqn (2)), take on the middle value, 45°. Then the frontier π-electron levels are disposed symmetrically with respect to the Fermi level; the charges on PC atoms alternate to a maximum degree both in the ground and excited states, with their ground-state magnitudes of opposite charges being equal; bond orders are completely equalized in both states (see Fig. 3). As the value of Φ_0 deviates from 45°, a bond-order alternation arises in the PC of PMD, enhancing with distance from its centre; the arrangement of shorter and longer bonds depends on whether high- or low-electron-donor EG are attached to the chain.

As with ideal polymethines, the frontier electron levels of ideal polyenes are symmetric relative to the Fermi level, thus corresponding to the middle electron donor ability, $\varphi_0 = 45°$. The distinction is that the symmetric level disposition in HP molecules is associated with the EG topological index Φ_0 equal to 0 or 90° and with a neutral polyenic form (*N*-form). Further, a quite different π-electron distribution over atoms and bonds of the PC occurs. The electron densities on atoms are equalized ($q_\mu = 1$) and the difference in the population of neighbouring bonds is maximal. On excitation, bond orders vary significantly, whereas atomic electron densities remain practically unchanged.

In conclusion, we have analysed the ground- and excited-state electronic structures of polymethine chains in polymethines and polyenes, focusing on substantial distinctions between the two basic types of linear polymethine compounds. Importantly, conditions for the existence of ideal polymethinic and polyenic states prove to be expressible in terms of the previously introduced end-group topological parameter, Φ_0, and the electron donor ability, φ_0. We anticipate that the relationships found will be helpful in further studies of electronic transitions in the systems concerned.

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