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Chemical Bond Analysis of Nonlinearity of Urea Crystal

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A novel and quantitative study on structure−property relationships has been carried out in urea crystal, based on the dielectric theory of complex crystals and the modified Levine bond charge model, mainly from the chemical bond viewpoint. For the first time, it was treated like this, and the bond parameters and linear and nonlinear characteristics of constituent chemical bonds were presented quantitatively. The theoretical result agrees satisfactorily with the experimental datum and can reasonably explain the nonlinear origin of urea crystal, that is, the C−N bond in the conjugated system of bonds $O \Leftarrow C \leftarrow N-H$. At the same time, the novel method should be a useful tool toward the future development of the search for new nonlinear optical (NLO) materials in the organic crystal field.

Introduction

Systematic structure−NLO (nonlinear optical) property investigations of classes of NLO materials are aimed at correlating structural properties to the nonlinear response with the ultimate goal of allowing "tuning" of the structure to enhance the nonlinear properties. In the search for new NLO materials for optoelectronic and photonic devices, conjugated organic molecules are the attractive candidates, as is exemplified by the large number of experimental and theoretical investigations devoted to them.[1−4] However, up to now, for medium to large size organic compounds, semiempirical[5−8] and advanced ab initio[9−13] quantum chemistry investigations have been much more successful in establishing trends in the NLO properties among a series of structurally related molecules rather than in predicting absolute hyperpolarizability values (i.e. d_{ij}). In this work, starting from the chemical bond viewpoint, we present a semiclassical study of optical nonlinearities in a prototype molecule, urea, which is a compound that has been thoroughly investigated both experimentally and theoretically.[14−20] Urea has the advantage of corresponding to a molecule that contains classic organic atoms and both single and double bonds; an accurate evaluation of its nonlinearities can then be helpful for future applications to the design of other interesting classes of organic nonlinear optical materials.

This paper calculates the nonlinearity of an organic crystal, urea, on the basis of the method[21] derived from the dielectric theory of complex crystals[22] and the Levine bond charge model,[23] which has been applied successfully to several important inorganic NLO crystals with H−O bonds. The calculation quantitatively gives the theoretical value of d_{36} that is in good agreement with experiment. This paper, in a sense, shows us that in the future NLO tensor coefficients of some organic nonlinear optical crystals with relatively smaller molecular weight can be evaluated by using our theoretical method.

Theory

When detailed information of the crystal structure is given, the subformula equation (the bond-valence equation)[22] of the crystal can be obtained according to the crystal formula. The subformula of any kind of chemical bond A−B in the multibond crystal $A_aB_bD_dG_g$... can be acquired by the following formula:

$$[N(B-A)a/N_{CA}]A[N(A-B)b/N_{CB}]B \tag{1}$$

In formula 1, A, B, D, G, ... represent different elements or different sites of the same element in the crystal formula, and *a*, *b*, *d*, *g*, ... represent numbers of the corresponding element, N(I−J) represents the number of ion I in the coordination group of ion J; N_{CA}, N_{CB}, ... represent the nearest coordination number of each element in the crystal.

After knowing bond structures of a complex crystal, we can list its crystal subformula equation and calculate each type of subformula by using the theory of complex crystals,[22] which was derived from the PV theory.[24,25] Any bond of type μ assumed in a complex crystal consists of A and B ions, the number of valence electrons of A and B are $Z^\mu{}_A$ and $Z^\mu{}_B$, respectively, the nearest coordination numbers of ions A and B are $N^\mu{}_{CA}$ and $N^\mu{}_{CB}$, respectively, and the effective charge of each valence electron of ions A and B are $q^\mu{}_A$ and $q^\mu{}_B$ (whose values can be determined by using the presented approach[22]), respectively. Here, we can obtain the effective valence electron of ions A and B:

$$(Z^\mu{}_A)^* = Z^\mu{}_A q^\mu{}_A \tag{2}$$

$$(Z^\mu{}_B)^* = Z^\mu{}_B q^\mu{}_B \tag{3}$$

The number of effective valence electrons per μ bond is

$$(n^\mu{}_e)^* = (Z^\mu{}_A)^*/N^\mu{}_{CA} + (Z^\mu{}_B)^*/N^\mu{}_{CB} \tag{4}$$

The bond volume $\nu^\mu{}_b$ for the bonds of type μ, as expected, is proportional to $(d^\mu)^3[\nu^\mu{}_b \propto (d^\mu)^3]$, where d^μ is the nearest-neighbor distance. For the case of the multibond, it is defined as

$$\nu^\mu{}_b = (d^\mu)^3/\sum_\mu (d^\mu)^3 N^\mu{}_b \tag{5}$$

where $N^\mu{}_b$ is the number of bonds of type μ per cubic centimeter, which can be obtained from the structure data of the crystal, where the denominator is the required normalized factor and the sum over μ runs over all the different types of bonds.

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The electron density associated with the bond μ is

$$(N^{\mu}_{e})^{*} = (n^{\mu}_{e})^{*}/\nu^{\mu}_{b} \qquad (6)$$

According to the PV theory, the susceptibility of any bond is written as

$$\chi^{\mu} = (4\pi)^{-1}(\hbar\Omega^{\mu}_{p}/E^{\mu}_{g})^{2} \qquad (7)$$

where E^{μ}_{g} is the average energy gap between the bonding and the antibonding states, and Ω^{μ}_{p} is the plasma frequency:

$$\Omega^{\mu}_{p} = [4\pi(N^{\mu}_{e})^{*}e^{2}/m]D_{\mu}A_{\mu} \qquad (8)$$

where D_{μ} and A_{μ} are the correction factors of order unity.[25]

We can separate E^{μ}_{g} into homopolar E^{μ}_{h} and heteropolar C^{μ} parts:

$$(E^{\mu}_{g})^{2} = (E^{\mu}_{h})^{2} + (C^{\mu})^{2} \qquad (9)$$

$$E^{\mu}_{h} = 39.74/(d^{\mu})^{2.48} \qquad (10)$$

$$C^{\mu} = 14.4b^{\mu}\exp(-k^{\mu}_{s}r^{\mu}_{0})\,[(Z^{\mu}_{A})^{*}/r^{\mu}_{0} - n(Z^{\mu}_{B})^{*}/r^{\mu}_{0}] \qquad (n \geq 1) \quad (11)$$

$$C^{\mu} = 14.4b^{\mu}\exp(-k^{\mu}_{s}r^{\mu}_{0})[(1/n)(Z^{\mu}_{A})^{*}/r^{\mu}_{0} - (Z^{\mu}_{B})^{*}/r^{\mu}_{0}] \qquad (n < 1) \quad (12)$$

where

$$k^{\mu}_{s} = (4k^{\mu}_{F}/\pi a_{B})^{1/2} \qquad (13)$$

$$k^{\mu}_{F} = [3\pi^{2}(N^{\mu}_{e})^{*}]^{1/3} \qquad (14)$$

and r^{μ}_{0} is the average radius of A and B in angstroms, equal half of the nearest-neighbor distance. In eq 13, a_{B} is the Bohr radius. In eqs 11 and 12, n is the ratio of numbers of the element B to A in the subformula, $\exp(-k^{\mu}_{s}r^{\mu}_{0})$ is the Thomas−Fermi screening factor, and b^{μ} is a correction factor and proportional to the pth power of the average coordination number N^{μ}_{C}. The detailed expressions are listed below:

$$b^{\mu} = \beta'(N^{\mu}_{C})^{2} \qquad (N^{\mu}_{C} \geq 3) \qquad (15)$$

$$b^{\mu} = \beta'(N^{\mu}_{C})^{3} \qquad (N^{\mu}_{C} < 3) \qquad (16)$$

$$N^{\mu}_{C} = N^{\mu}_{CA}/(1+n) + nN^{\mu}_{CB}/(1+n) \qquad (17)$$

If the index of refraction or the dielectric constant for the crystal is known, the value of the proportionality constant β' can be deduced from the above equations.

If the crystal is composed of different types of bonds (labeled μ), then the total χ can be resolved into contributions χ^{μ} from the various types of bonds,

$$\chi = \sum_{\mu} F^{\mu}\chi^{\mu} = \sum_{\mu} N^{\mu}_{b}\chi^{\mu}_{b} \qquad (18)$$

where χ^{μ} is the total macroscopic susceptibility that a crystal composed entirely of bonds of type μ would have. F^{μ} is the fraction of bonds of type μ composing the actual crystal; χ^{μ}_{b} is the susceptibility of a single bond of type μ.

We can determine the fractional ionicity f_{i}^{μ} and covalency f_{c}^{μ} of the individual bonds,

$$f_{i}^{\mu} = (C^{\mu})^{2}/(E^{\mu}_{g})^{2}, \quad f_{c}^{\mu} = (E^{\mu}_{h})^{2}/(E^{\mu}_{g})^{2} \qquad (19)$$

In single-bond crystals, the bond nonlinearity had been evaluated on the basis of the linear results by means of the two-band quantum-mechanical model of Phillips and Van Vechten (PV)[26,27] and the bond charge model of Levine.[23] The corresponding macroscopic properties are the SHG coefficients d_{ijk} and the Miller delta Δ_{ijk}. In multibond crystals, the complete expression for the total nonlinear susceptibility d_{ijk} can be written as[23]

$$d_{ijk} = \sum_{\mu} F^{\mu}d^{\mu}_{ijk} = \sum_{\mu} F^{\mu}[d^{\mu}_{ijk}(C) + d^{\mu}_{ijk}(E_{h})] \qquad (20)$$

or

$$\beta = \sum_{\mu} \beta^{\mu} = \sum_{\mu} F^{\mu}d^{\mu}_{ijk}/G^{\mu}_{ijk}N^{\mu}_{b} \qquad (20')$$

where d^{μ}_{ijk} is the total macroscopic nonlinearity that a crystal composed entirely of bonds of type μ would have, $d^{\mu}_{ijk}(C)$ is the ionic fraction of the nonlinear optical coefficient, and $d^{\mu}_{ijk}(E_{h})$ is the covalent fraction.

$$F^{\mu}d^{\mu}_{ijk}(C) = \frac{G^{\mu}_{ijk}N^{\mu}_{b}(14.4)b^{\mu}\exp(-k^{\mu}_{s}r^{\mu}_{0})[(Z^{\mu}_{A})^{*} + n(Z^{\mu}_{B})^{*}](\chi^{\mu}_{b})^{2}C^{\mu}}{(E_{g})^{2}(d^{\mu})^{2}q^{\mu}} \qquad (21)$$

$$F^{\mu}d^{\mu}_{ijk}(E_{h}) = \frac{G^{\mu}_{ijk}N^{\mu}_{b}(2s-1)[r^{\mu}_{0}/(r^{\mu}_{0} - r^{\mu}_{c})]^{2}f^{\mu}_{c}(\chi^{\mu}_{b})^{2}\rho^{\mu}}{d^{\mu}q^{\mu}} \qquad (22)$$

G^{μ}_{ijk} the geometrical contribution of the bonds of type μ, which can simply be calculated from

$$G^{\mu}_{ijk} = 1/n^{\mu}_{b}\sum_{\lambda} \alpha^{\mu}_{i}(\lambda)\,\alpha^{\mu}_{j}(\lambda)\,\alpha^{\mu}_{k}(\lambda) \qquad (23)$$

where the sum on λ is over all n^{μ}_{b} bonds of type μ in the unit cell, and $\alpha^{\mu}_{i}(\lambda)$ is the direction cosine with respect to the ith coordinate axis of the λth bond of type μ in the unit cell. The difference in the atomic sizes $\rho^{\mu} = (r^{\mu}_{A} - r^{\mu}_{B})/(r^{\mu}_{A} + r^{\mu}_{B})$, r^{μ}_{A} and r^{μ}_{B} are the covalent radii of atoms A and B, and the values of r^{μ}_{B} are taken from ref 28. Taking the bond length d^{μ} into account, then we can get $r_{A} = d - r_{B}$, and d is the shortest bond length among all chemical bonds of this A−B type. r^{μ}_{0} is the average radius of A and B in angstroms, r^{μ}_{c} is the core radius, and $r^{\mu}_{c} = 0.35r^{\mu}_{0}$. q^{μ} is the bond charge of the μth bond,

$$q^{\mu} = (n^{\mu}_{e})^{*}[1/(\chi^{\mu} + 1) + Kf^{\mu}_{c}]e \qquad (24)$$

K is a function of the crystal covalency F_{c}, and its best value can be determined by using the following equation:[21]

$$K = 2^{F_{c}} - 1.1 \qquad (25)$$

where F_{c} is defined as

$$F_{c} = \sum_{\mu} N^{\mu}_{b}f_{c}^{\mu} \qquad (26)$$

Since Miller's[29] Δ_{ijk} is normalized to the linear susceptibility, it is more closely related to the intrinsic crystalline acentricity than d_{ijk}; therefore, Δ_{ijk} is a useful representation for the nonlinear susceptibility. It is defined by[29]

$$\Delta_{ijk} = d_{ijk}/\chi_i(2\omega_i)\,\chi_j(\omega_j)\,\chi_k(\omega_k) \tag{27}$$

where ω_i are the appropriate optical frequencies involved, and $\chi_i(2\omega_i)$ is the appropriate susceptibility at $2\omega_i$. However, when we calculate the Δ_{ijk} value, its approximate form is always introduced as following

$$\Delta_{ijk} = d_{ijk}/\chi_i(\omega_i)\,\chi_j(\omega_j)\,\chi_k(\omega_k) \tag{28}$$

Further, we have

$$\Delta_{ijk} = \sum_{\mu} F^{\mu}\Delta^{\mu}{}_{ijk} = \sum_{\mu} F^{\mu}[\Delta^{\mu}{}_{ijk}(C) + \Delta^{\mu}{}_{ijk}(E_{\mathrm{h}})] \tag{29}$$

$$F^{\mu}\Delta^{\mu}{}_{ijk}(C) = \frac{G^{\mu}{}_{ijk}N^{\mu}{}_{\mathrm{b}}(14.4)b^{\mu}\exp(-k^{\mu}{}_{\mathrm{s}}r^{\mu}{}_{0})[(Z^{\mu}{}_{\mathrm{A}})^{*} + n(Z^{\mu}{}_{\mathrm{B}})^{*}](\chi^{\mu}{}_{\mathrm{b}})^{2}C^{\mu}}{(E_{\mathrm{g}})^{2}(d^{\mu})^{2}q^{\mu}\chi^{3}} \tag{30}$$

$$F^{\mu}\Delta^{\mu}{}_{ijk}(E_{\mathrm{h}}) = \frac{G^{\mu}{}_{ijk}N^{\mu}{}_{\mathrm{b}}(2s-1)[r^{\mu}{}_{0}/(r^{\mu}{}_{0} - r^{\mu}{}_{\mathrm{c}})]^{2}f^{\mu}{}_{\mathrm{c}}(\chi^{\mu}{}_{\mathrm{b}})^{2}\rho^{\mu}}{d^{\mu}q^{\mu}\chi^{3}} \tag{31}$$

In the denominators of eqs 30 and 31, χ is the total macroscopic susceptibility. The Δ_{ijk} equation is useful since in our calculation we use the extrapolated low−frequency electronic susceptibility χ, whereas the experimentally measured nonlinearity may include a significant amount of dispersion. As is well-known,[30] the effects of dispersion on Δ_{ijk} are less pronounced than those for d_{ijk}, and hence for a meaningful comparison between our theory and experiment it is appropriate to use Δ_{ijk}. Therefore, the value of d_{ijk} calculated from the theory does not account for frequency dispersion.

Results and Discussion

At room temperature, urea crystals belong to the space group $I\bar{4}2_1m$, which belong to the class $\bar{4}2m$ of the tetragonal system. The unit dimensions for urea are $a = b = 5.661$ Å, $c = 4.712$ Å. There are 2 formula-units per cell.[31] As shown in Figure 1, any molecule in the crystal is connected to six neighboring ones by eight hydrogen bonds. Hydrogen bond lengths are respectively 2.06 Å for the four bonds connecting the "central" molecule to its four neighbors located at right angles and 2.08 Å for the four bonds connecting with the two molecules located in the same plane. Therefore, molecules located within the same column are more tightly bonded than those in orthogonal planes.

The symmetry restrictions on the nonlinear polarization at the second harmonic frequency are the same as those for piezoelectricity, and in terms of the fundamental optical electric fields along the principal axes the components of the polarization are given by[32,33]

$$P_x = 2d_{14}E_yE_z \tag{32}$$

$$P_y = 2d_{14}E_zE_x \tag{33}$$

$$P_z = 2d_{36}E_xE_y \tag{34}$$

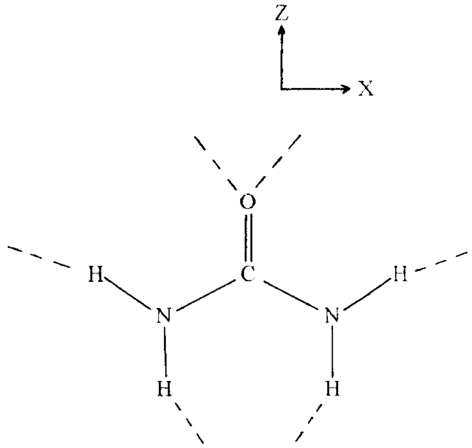

Figure 1. Geometric structure and chemical bonding of the urea molecule. - - - indicates the hydrogen bonding H- - -O.

TABLE 1: Theoretical Results of Bond Parameters and Linear and Nonlinear Properties of Each Type of Constituent Chemical Bonds in Urea Crystal[a,b]

	C−O	C−N	H(1)−N	H(1)−O	H(2)−N	H(2)−O
d^{μ}	1.2430	1.3511	0.9884	2.0622	0.9951	2.0800
E_{h}^{μ}	23.1707	18.8418	40.9067	6.6022	40.2271	6.4630
C^{μ}	24.3684	5.7386	7.9325	9.5478	7.8425	9.3892
f_{c}^{μ}	0.4748	0.9151	0.9638	0.3235	0.9634	0.3215
$4\pi\chi^{\mu}$	0.7945	3.4517	0.6810	0.6323	0.6904	0.6393
χ_{b}^{μ}	0.4340	1.8853	0.3720	0.3454	0.3771	0.3492
ρ^{μ}	0.0282	0.1873	−0.1113	−0.1582	−0.1113	−0.1582
q^{μ}/e	2.1191	3.0320	1.9142	1.0325	1.9080	1.0277
β^{μ}	−0.0107	−0.6587	0.0395	0.0202	0.0404	0.0205
G_{36}^{μ}	0.0000	−0.1899	−0.1847	0.1262	0.0018	−0.1174
$F^{\mu}\Delta_{36}^{\mu}$	0.0000	3.9988	−0.2330	0.0815	0.0023	−0.0770
$F^{\mu}d_{36}^{\mu}$	0.0000	3.3138	−0.1931	0.0675	0.0019	−0.0638

[a] The units used for each parameter are d^{μ} (Å), E_{h}^{μ} (eV), C^{μ} (eV), $F^{\mu}\Delta_{36}^{\mu}$ (10^{-6} esu), and $F^{\mu}d_{36}^{\mu}$ (10^{-9} esu). [b] Four significant digits are used in this table. Since all values listed here are calculated from structural data, all of these structural values are four significant digits, so our results have this level of accuracy.

where the symmetry conditions of Kleinman[33] require $d_{14} = d_{36}$, so there is only one independent tensor component, d_{36}.

In section 1 we have demonstrated a method for decomposing the complex crystal formula with the detailed structure information and the method given above, we can directly obtain the bond-valence equation of the urea crystal, i.e.,

$$\mathrm{CO(NH_2)_2} = {}^{1}\!/_{3}[\mathrm{CO_{3/5}}] + {}^{2}\!/_{3}[\mathrm{CN}] + \mathrm{H(1)N_{2/3}} + \mathrm{H(1)O_{2/5}} + \mathrm{H(2)N_{2/3}} + \mathrm{H(2)O_{2/5}} \tag{35}$$

According to the detailed bond structure of each type of bond, the effective valence electron of constituent ions can be obtained as follows: For C−O bonds, $Z_{\mathrm{C}}^{*} = 2.00$ and $Z_{\mathrm{O}}^{*} = 10.00$; for C−N bonds, $Z_{\mathrm{C}}^{*} = 5.00$ and $Z_{\mathrm{N}}^{*} = 8.33$; for H−N bonds, $Z_{\mathrm{H}}^{*} = 1.33$ and $Z_{\mathrm{N}}^{*} = 3.33$; and for H−O bonds, $Z_{\mathrm{H}}^{*} = 0.67$ and $Z_{\mathrm{O}}^{*} = 5.00$. Using the index of refraction of urea crystal (there are two indices of refraction: n_Z along the C═O bond axis is 1.5825, and $n_X = n_Y = 1.4766$,[20] when $\lambda = 1.064$ μm; in this paper, $n_X = n_Y = 1.4766$ is used neglecting the dispersion), we can get all bond parameters and linear and nonlinear characteristics of its constituent bonds, which are tabulated in Table 1.

In Table 1, we can see that in this conjugated organic molecule values of the fractional covalency f_c^{μ} of the individual bonds in the conjugated system O⇐C←N−H are increasing clearly from 0.4748 to 0.9638, with the length of the conjugated chain increasing; that is, the influence of the O element with

TABLE 2: Comparisons of Theoretical Calculations and Experimental Data on the Urea Crystal

	expt		calc			
	ref 14	ref 20	ref 19	ref 18	ref 17	this work
d_{36}($\times 10^{-9}$ esu)	3.4	3.34	1.7−2.5	2.3−7.1	4.4, 6.9	3.1263

high electronegativity on other elements in the conjugated system $O \Leftarrow C \leftarrow N-H$ is becoming weaker and weaker, with the distance between oxygen and the other element increasing.

Form Table 1, we can find that C−N bonds are the most important parts in this crystal; they have overwhelming linear and nonlinear contributions to the total linearity and nonlinearity of the urea crystal. It is advantageous for this kind of bond that they have relatively larger geometrical factors $G_{ijk}^{\mathrm{C-N}}$ than other kinds of bonds. Therefore, the origin of its nonlinearity is from the C−N bonds. We also can see that H−O bonds in this crystal unlike those in the inorganic crystals[21] are intermolecular bonds and are not as significant as previously thought. These results on the hydrogen bonds agree with those of Perez and Dupuis,[18] who have made ab initio SCF calculations of the (hyper)polarizability tensors of the urea molecule. Our calculations also show that the influence of "parallel" hydrogen bonds directed along z is greater on the polarizability tensor than that of "perpendicular" bonds.[17]

From Table 2, we can see that of all the theoretical calculations on the nonlinearity of this organic crystal, our method can present us a satisfactory prediction based on the crystal structure. Furthermore, the linear electro-optic coefficient r_{36} can be calculated by using the relation[34,35] $r_{ijk} = -8\pi d_{ijk}/n_i^2 n_j^2$, neglecting the local dc field correction and dispersion; that is, $r_{36} = r_{41} \approx -1.6528 \times 10^{-8}$ esu. This is the nearly same value as that of Morrell et al.,[35] $|r_{41}| = 1.5 \times 10^{-8}$ esu and $|r_{36}| = 1.6 \times 10^{-8}$ esu, which was calculated by using CNDO/S.

Conclusion

In this paper, the origin of the nonlinearity of the organic crystal, urea, has been shown from the chemical bond standpoint, and all the constituent chemical bonds have been scaled by the parameters. Theoretical results successfully agree with the observed ones, and this method gives us a new powerful tool in searching for new nonlinear optical materials. However, such bond networks with delocalized bond charge as those found in conjugated linear polyenes and cyanines cannot be solved currently by using this theory, since the Levine model assumes chemical bonds with localized bond charge. Therefore, further research on this field holds very much interest.

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Appendix

In eqs 15 and 16, β' is only a proportional constant; its value can be deduced from the following formula:

$$(\beta')^2 = \frac{(n_r^{\,2} - 1)^{-1}\sum_\mu (\hbar\Omega_p^{\,\mu})^2 - \sum_\mu [39.74/(d^\mu)^{2.48}]^2}{\{\sum_\mu 14.4(N_C^{\,\mu})^x \exp(-k_s^{\,\mu} r_0^{\,\mu})[(1/n)(Z_A^{\,\mu})^*/r_0^{\,\mu} - (Z_B^{\,\mu})^*/r_0^{\,\mu}]\}^2} \quad (36)$$

where $x = 2$ or 3, depending on the value of $N_C^{\,\mu}$. The sum over μ runs over all the different types of bonds in the unit cell.

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