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Charge distortion by sparkles can explain strong SHG by centrosymmetric squaraine dyes

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Ashwell and his co-workers have published a report describing second harmonic generation (SHG) from a laser beam (Nd:YAG, 1.064 μm) by a Langmuir–Blodgett (LB) monolayer of a symmetrically substituted diaryl squaraine dye. The molecular geometry of the squaraine, and its unit cell is known to be centrosymmetric in the crystalline state. It has been stated that interfacial effects (arising from the twin-step function in the refractive index) cannot account for the magnitude of the observed SHG. It has also been assumed that molecular centrosymmetry has been retained in the LB film, with the observed SHG being attributed to the presence of non-centrosymmetric ensembles of these centrosymmetric molecules.

We show that an electronically distorted (and therefore non-centrosymmetric) squaraine molecule can exhibit large SHG coefficients, these distortions being induced by the proximity of the highly polar species that constitute the molecular environment. In our model of a T-shaped dimer, both monomer components become non-centrosymmetric, the mutual interaction between the two monomers being modelled by using a negative or a positive sparkle. We attribute the noteworthy SHG output from LB films of Ashwells centrosymmetric squaraines to intramolecular charge transfer within the distorted monomers in the T-dimer.

Second harmonic generation (SHG) by an electric dipole mechanism is not possible in a centrosymmetric medium. Thus, non-centrosymmetric molecules have usually been chosen when preparing organic systems for the study of SHG. However, Ashwell *et al.* have now shown that squaraine molecules that are centrosymmetric in the crystalline state can exhibit SHG[1,2] when deposited as thin, compressed films, and the occurrence of non-centrosymmetric ensembles in Langmuir–Blodgett films of tetra-alkyl squaraines has been invoked as the cause of these unexpected results. A centrosymmetric bonding structure has been assumed to be present in the monomers comprising these ensembles,[1] and emphasis has been placed upon contributions from intermolecular charge transfer as the principal cause of the large magnitude of the observed SHG.[2] We show that non-centrosymmetric monomers[3] created by intermolecular electric fields can be present in dimeric ensembles, and that vector addition of the intramolecular charge transfer contributions to the SHG from these distorted monomers can help interpret Ashwell's observations.[4]

All expressions for the electric dipole mechanism[5,6] for halving the wavelength of incident light (second harmonic generation, SHG) involve the ground state (O), the electric dipole operators ($\mathbf{r}_1$, $\mathbf{r}_2$, $\mathbf{r}_3$) and excited states (a, b) in a triple-product of matrix elements of general form $<\mathrm{O}|\mathbf{r}_1|a>$ $<a|\mathbf{r}_2|b>$ $<b|\mathbf{r}_3|\mathrm{O}>$. In the presence of a centre of inversion symmetry, O is classified as even (gerade) and all $\mathbf{r}_i$ are odd (ungerade). By the Laporte Parity Rule,[7] a and b must both be odd if the first and last matrix elements are to be overall even (and thereby non-zero on symmetry grounds). Consequently, the matrix element $<a|\mathbf{r}_2|b>$ is odd and must be zero. Therefore a material can only exhibit SHG (by an electric dipole mechanism) if it is constituted of ensembles or unit cells that are non-centrosymmetric.

Awareness of this rigorous rule has brought about the extensive use of non-centrosymmetric molecules in the design of SHG-active organic solids, despite the fact that such molecules often pack to give centrosymmetric unit cells, thereby destroying the sought-after SHG.[8]

There was a dramatic break from this tradition when Ashwell and his co-workers[1] published their exciting and thought-provoking finding that squaraine molecules of proven centrosymmetric structure in the crystalline state exhibit second harmonic generation of laser light when deposited as Langmuir–Blodgett films. Two means by which the centrosymmetry of the squaraine monomers can be destroyed have already been considered; namely, the step-function in the refractive index represented by the substrate–organic–air interfaces and the formation of non-centrosymmetric aggregates.[1,2] Attention has focused upon acentric aggregation because the magnitude of the observed SHG (and its partial retention when the LB layers are deposited upon an inactive organic Langmuir–Blodgett underlayer)[4] is too large to be attributed to an interfacial step function. Magnetic dipole and electric quadrupole mechanisms have also been discounted, in the case of these squaraines, because the observed effect is so large.[1]

There is a mechanism by which the centre of inversion symmetry in the monomeric squaraine chromophore can be destroyed; this mechanism involves asymmetric distortion of the charge distribution in the monomer by the highly polar molecular environment. It is the origin and effect of this distortion that constitute the theme of this paper.

Structures of monomeric squaraines

Centrosymmetric monomers

The structure of the centrosymmetric form of the squaraine chromophore (I) is conventionally depicted as shown in Fig. 1. Although this is consistent with the lack of characteristic C=O bond-stretching frequency in the infra-red spectrum, it does not account for the quinonoid-like alternation of bond lengths exhibited by the donor parts of the molecule. Inclusion of four equivalent hemiquinonoidal structures [summarised as II, Fig. 1] takes account of the observed bond-length alternation (BLA). Structures I and II respectively depict the ‘aromatic’ and ‘quinonoidal’ forms of the centrosymmetric monomer. Bigelow and Freund[9] have performed a detailed theoretical study of the centrosymmetric squaraine structure and found that, by modelling the presence of polar solvent by the

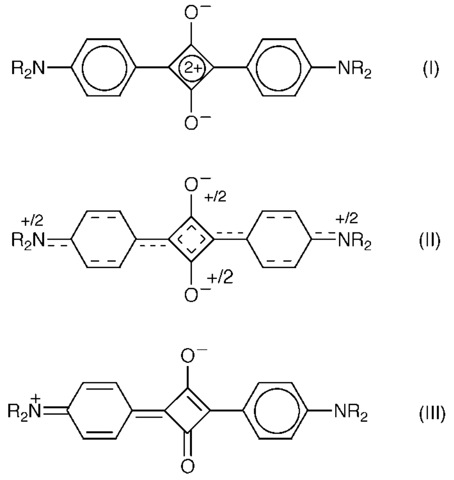

Fig. 1 Bonding structures of bis(4-alkylaminophenyl)squaraine dyes. I: centrosymmetric aromatic form; II: centrosymmetric partially quinonoid form; III: non-centrosymmetric form with quinonoid and aromatic regions. R = H or CH_3 in our calculations.

inclusion of centrosymmetrically positioned sparkles, a polar medium enhanced the BLA, stabilised the quinonoidal form and retained the centrosymmetry. We therefore suggest that the presence of O^- centres within adjacent molecules in the polar medium of a Langmuir–Blodgett film of a squaraine dye will have a similar effect, with the exception that there are few locations for the O^- centres that will retain centrosymmetry in an adjacent, and consequently perturbed molecule.

Non-centrosymmetric monomers

Researchers engaged in technical, commercial applications of squaraine dyes (especially solid-state electrophotography and optical storage) frequently use the non-centrosymmetric hemiquinonoid structure III (Fig. 1), and a range of theoretical methods have been applied to dyes to which this structure has been assigned,[10–13] even when the pattern of substitution is ‘symmetrical’. In the context of predicting the energies of the lower excited states of squaraines[10–13] and a range of planar, conjugated donor–acceptor dyes[14,15] other workers have found that the π-electrons-only (SCF-PPP-CI) method proffered greater predictive facility than all-valence-electron methods.

Structures of dimeric squaraines

Squaraine dyes are donor–acceptor–donor systems, and the centrosymmetric monomer is usually depicted D–A–D. The non-centrosymmetric monomer can be depicted as $D^+{=}A^-{-}D$ (*cf.* III). Both these monomers can form four centrosymmetric dimers (two face-to-face and two in-plane (Fig. 2)). When these dimers are displaced along their molecular axes, dimers exhibiting pronounced SHG will not be obtained because a vectorial property will either cancel completely, or cancel to a substantial extent. Ashwell *et al.*[16] have observed a distorted T-shape dimer in the solid state and have stated that the individual chromophores are centrosymmetric. We have adopted a perfect T-shaped dimer of coplanar monomers (which are initially centrosymmetric) for our calculations (Fig. 3). The closest intermolecular O–N separation is denoted as *R*. In the absence of *N*-alkyl groups, the minimum value of $R \sim 0.25$ nm is determined by the geometry of the hydrogen-bonded HNHO rhombohedron. In the tetra-*n*-butyl compound the closest intermolecular contact[16] of 0.3382 nm is between an oxygen atom and the carbon atom of the 1-CH_2 unit of an *N*-*n*-butyl substituent. Even in compressed films of squaraines with small *N*-alkyl groups we suggest that $R \geqslant 0.35$ nm.

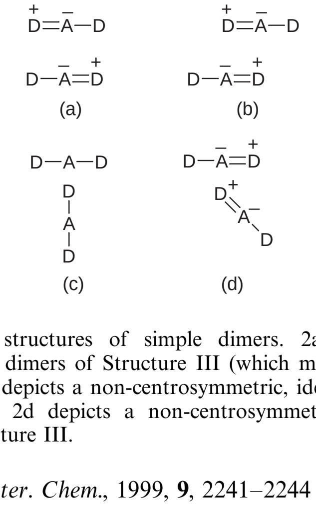

Fig. 2 Idealised structures of simple dimers. 2a and 2b depict centrosymmetric dimers of Structure III (which may be face-to-face or coplanar). 2c depicts a non-centrosymmetric, idealised T-dimer of Structure I and 2d depicts a non-centrosymmetric and distorted T-dimer of Structure III.

Bigelow and Freund[9] modelled the influence of solvent-oxygen atoms upon squaraine dyes by the use of sparkles in the MNDO formalism. Using the same formalism we have modelled the influence of an O^- centre upon the T-stem monomer by placing a unit-charged negative sparkle on the long molecular axis at a distance $R = 0.35$ nm. In contrast to Bigelow and Freund,[9] we have applied an asymmetric perturbation and the perturbed molecule has become non-centrosymmetric. The donor region in the T-stem monomer adjacent to the O^- (or sparkle) is now markedly quinonoid, whereas the remote donor region is rendered more aromatic; the differing extents of bond-length alternation (shown in Fig. 3) serve to highlight this point. As a consequence, the donor region in the T-stem monomer adjacent to the T-cross monomer can now be regarded as having an $=N^+R_2$ centre, and we have therefore modelled the perturbation of the T-cross monomer by placing a unit-charged positive sparkle on the short molecular axis at a distance $R = 0.35$ nm from the adjacent oxygen atom. The outcome is that the dimer (IV) and both monomers are all, individually, non-centrosymmetric (Fig. 3), although reflection symmetry about the molecular (*xy*) and *yz* planes is maintained. Thus, intramolecular charge transfer within both monomers can now contribute to SHG, for which only dipole moments and transition moments in the *y*-direction need be considered for a non-distorted T-shape. Dibella *et al.* have

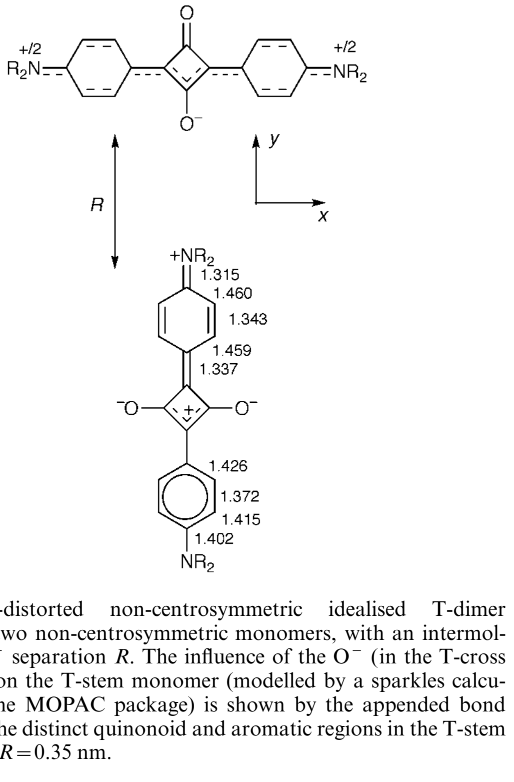

Fig. 3 Charge-distorted non-centrosymmetric idealised T-dimer consisting of two non-centrosymmetric monomers, with an intermolecular N^+–O^- separation *R*. The influence of the O^- (in the T-cross monomer) upon the T-stem monomer (modelled by a sparkles calculation using the MOPAC package) is shown by the appended bond lengths: note the distinct quinonoid and aromatic regions in the T-stem monomer for $R = 0.35$ nm.

recently reported that a geometrically centrosymmetric dimeric cationic (charge-injected) ensemble exhibits a substantial dipole moment and SHG by virtue of a non-centrosymmetric distribution of charge.[17] This is similar to the influence of sparkles upon geometrically centrosymmetric species that we have just described.

Calculation of the β-tensor for SHG

The MNDO geometry and π-electron charge density distribution obtained from the calculations using positive or negative sparkles were used to assign the most appropriate bonding structure for each monomer (T-cross and T-stem) (*cf.* Fig. 3), which in turn affected the choice of parameters for the oxygen and nitrogen atoms. The core charges, ionisation potentials, electron affinities and Slater exponents for O^- and N^+ differ from those for O and N.[3] Griffiths has given a detailed list of parameters for use in SCF PPP calculations on squaraines[10] and the Slater exponents[18] for O^- and N^+ are 2.10 and 2.125 (these last are used in our CNDO/S calculations).

All-valence electron calculations (including MNDO[10] and CNDO/S[12]) on squaraine dyes give excitation energies that are too high and Bigelow and Freund needed to introduce a substantial post-calculation correction factor.[9] Within the SCF PPP CI approximation, the use of a carefully selected set of parameters (such as those of Griffiths,[10] or modifications thereof[13]) gives good agreement with experiment. For example, the calculated energy of the first excited singlet state of a centrosymmetric squaraine monomer ($R=H$ or CH_3) lies close to the value observed in solution. We have adopted the SCF PPP CI method to evaluate the energy of the 25 lowest energy singlet excited state using configuration interaction between the 25 lowest energy one-electron excitations. We find that a red shift of 50–70 nm is predicted in the first excited state of the non-centrosymmetric monomers (compared to the centrosymmetric monomers). We have used the set of excited states, as described elsewhere[19,20] to evaluate $\beta(-2\omega,\omega,\omega)$, the SHG tensor, by the sum-over-states (SOS) method. The non-distorted T-dimer (Fig. 3) retains mirror symmetry about the *xy* and *yz* planes. This determines that all tensor components are zero except for $\beta_y=\beta_{yyy}+(\beta_{yxx}+\beta_{xyx}+\beta_{xxy})/3$. Our results show that β_y is dominated by contributions from the transfer of charge between the two oxygen atoms in the T-cross monomer and the transfer of charge along the long molecular axis of the T-stem monomer, with the latter being approximately 35 times larger than the former in absolute magnitude. These two contributions are opposite in sign. Using Griffith's parameters,[10] we find that for the idealised T-dimer (Fig. 3) $\beta(-2\omega,\omega,\omega)$ is 676×10^{-30} cm^5 esu^{-1} at a laser wavelength of 9900 nm, rising to 1590×10^{-30} cm^5 esu^{-1} at a laser wavelength of 990 nm as the resonance condition[19] $\omega_{no}=2\omega$ is approached, in which ω_{no} represents the energy of the first excited electronic state. For comparative purposes, it is preferable to use values in the far pre-resonance region, and we note that the non-distorted T-dimer has calculated values of $\beta(-2\omega,\omega,\omega)$ higher than an extensive range of donor–acceptor dyes.[19]

Our results show that over 95% of the contributions to $\beta(-2\omega,\omega,\omega)$ come from the first excited state and that 98% of this state is contributed by the one-electron transition between the highest occupied and lowest empty molecular orbitals. Thus, the two-state model as described by Pugh and Morley[20] can be applied. The values for second harmonic generation, $\beta^{CT}(-2\omega,\omega,\omega)$, the Pockels effect, $\beta^{CT}(-\omega,\omega,0)$ and signal mixing, $\beta^{CT}(-\omega_3,\omega_1,\omega_2)$ that we obtain by applying the two-state model (the superscript 'CT' signifies this Charge Transfer approximation) to structure III in both the near and far pre-resonant regions are given in Table 1. The expressions for the above three β^{CT}-tensors are as follows:

$$\beta^{CT}(\omega,\omega,0)=2\xi(3\omega_{no}{}^2-\omega^2)/(\omega_{no}{}^2-\omega^2)$$

$$\beta^{CT}(-\omega_3,\omega_1,\omega_2)=$$

$$\frac{\xi.\ [3\omega_{no}{}^4-\omega_{no}{}^2(\omega_1{}^2+\omega_2{}^2\pm\omega_1\omega_2)]}{(\omega_{no}{}^2-\omega_2{}^2)\ (\omega_{no}{}^2-\omega_1{}^2)\ (\omega_{no}{}^2-\omega_1{}^2-\omega_2{}^2\pm2\omega_1\omega_2)}$$

$$\beta^{CT}(-2\omega,\omega,\omega)=1.5\xi\omega_{no}{}^2/[(\omega_{no}{}^2-4\omega^2)\ (\omega_{no}{}^2-\omega^2)]$$

$$\xi=4\pi^2e^3\ (r_{no}{}^y)^2\ (\Delta r_{no}{}^y)/h^2$$

in which e is the unit of electronic charge, *h* is Planck's constant, and $r_{no}{}^y$ and $\Delta r_{no}{}^y$ are the transition moment and change in molecular dipole moment in the *y*-direction for the CT transition with frequency ω_{no}. In $\beta^{CT}(-\omega_3,\omega_1,\omega_2)$, the upper signs are for summation of the incident frequencies, and the lower signs for their difference.

The simplest distortion of the idealised T-dimer is to maintain co-planarity whilst deflecting the T-stem monomer by an angle θ. The mutual perturbations that arise at larger values of θ will cause both monomers to adopt a hemiquinonoid form (structure III). In this circumstance, and with $\theta=90°$, the SHG effect is zero by symmetry. However, with $\theta=45°$, the lower symmetry dictates that β_y and $\beta_x=\beta_{xxx}+(\beta_{xyy}+\beta_{yxy}+\beta_{yyx})/3$ are now both non-zero, and the joint effect of intramolecular charge transfer along both pairs of molecular axes gives, by vector addition, a value for $\beta(2\omega,\omega,\omega)$ of 582×10^{-30} cm^5 esu^{-1} in the far pre-resonant region.

Although the CNDO/S method has proved to be unsatisfactory for predicting the optical spectra of large dye molecules,[10,12] we have adopted it for assessing the extent of intermolecular charge transfer in the distorted T-dimers. Our CNDO/S results show little evidence for intermolecular charge transfer, presumably because the two component monomers are coplanar. We have thus been enabled to reveal the highly significant role of intramolecular charge transfer in the context of SHG by squaraine dimers. In the squaraines being studied by Ashwell *et al.*,[21] the steric influence of the alkyl groups will cause the monomers to be mutually non-coplanar, thereby giving some degree of interfacial interaction. This last is lacking in the T-dimers utilised in our present work. Bulky

Table 1 Calculated values of second-order optical properties within the two-state approximation of a charge distorted monomer of the tetra-*N*-methyl squaraine. Detailed expressions for the β tensors can be found elsewhere.[19,20] Values shown can be converted to SI units (cm^3 V^{-2}) by use of the factor 3.7114×10^{-21}

		Laser wavelength	
Calculated tensor component	Experimental effect	Far preresonance $\lambda=9900$ nm (/10^{-30} cm^5 esu^{-1})	Near preresonance $\lambda=990$ nm (/10^{-30} cm^5 esu^{-1})
$\beta^{CT}(-\omega,\omega,0)$	Pockels	345	602
$\beta^{CT}(-\omega_3,\omega_1,\omega_2)$	Signal mixing (sum)	149	255
	Signal mixing (diff)	163	283
$\beta^{CT}(-2\omega,\omega,\omega)$	Second harmonic generation	738	1750

alkyl groups will lead to greater values of R and cause a diminution of such intermolecular effects as intermolecular charge transfer and the charge distortion (as described above) that creates the possibility of intramolecular charge transfer and its attendant influence upon non-linear optical properties. Ashwell *et al.*[21] have noted a ten-fold reduction in the magnitude of SHG by squaraines as the alkyl group is changed from *n*-butyl to *n*-docosyl.

Conclusion

We have shown that charge distortions imposed upon a geometrically centrosymmetric framework can induce overall non-centrosymmetry in squaraine monomers. These monomers can exhibit substantial SHG, the mechanism being dominated by extensive intramolecular charge transfer. Non-centrosymmetric dimers, composed of these charge-distorted monomers, can also exhibit substantial SHG, the mechanism for which involves intramolecular (NOT intermolecular) charge transfer. Vector algebra can be used to combine the contributions from the two charge-distorted monomers. Our results imply that the observed red shift of the *circa* 630 nm band when going from solution to compressed film or crystalline solid has a substantial component from modified intramolecular charge transfer. Runser *et al.*[22] have noted the profound effect of the polarity of a medium upon intramolecular charge transfer in zwitterions which, in turn, affected the bond-length alternation and the quadratic hyperpolarisability (SHG).

References

1 G. J. Ashwell, G. Jefferies, D. G. Hamilton, D. E. Lynch, M. P. S. Roberts, G. S. Bahra and C. R. Brown, *Nature*, 1995, **375**, 385.

2 G. J. Ashwell, *Adv. Mater.*, 1996, **8**, 248; G. J. Ashwell, P. C. Williamson, G. S. Bahra and C. R. Brown, *Aust. J. Chem.*, 1999, **52**, 37.

3 C. L. Honeybourne, *Int. Symp. Materials for Modern Communication Systems*, St. Andrew's, July 1996, 4.

4 G. J. Ashwell, G. M. S. Wong, D. G. Bucknall, G. S. Bahra and C. R. Brown, *Langmuir*, 1997, **13**, 1629; G. J. Ashwell, *J. Mater. Chem.*, 1998, **8**, 373.

5 C. L. Honeybourne, *J. Phys. D*, 1990, **23**, 245.

6 B. K. Nakar and C. S. Winter, *Opt. Quantum Electron.*, 1990, **22**, 297.

7 W. Kauzmann, *Quantum Chemistry: an Introduction*, Academic Press, New York, 1987, p. 661.

8 J. Zyss and D. S. Chemla, in *Nonlinear Optical Properties of Organic Molecules* (Ed. D. S. Chemla and J. Zyss), Vol. 1, Academic Press, Orlando, 1987, pp. 23–191.

9 R. W. Bigelow and H. J. Freund, *Chem. Phys.*, 1986, **107**, 159.

10 L. B. Cheng, X. Chen, Y. F. Hou and J. Griffiths, *Dyes Pigm.*, 1989, **10**, 123.

11 K. A. Bello, S. N. Corns and J. Griffiths, *J. Chem. Soc., Chem. Commun.*, 1993, 442.

12 C. W. Kirk, W. C. Herndon, F. Cervantes-Lee, H. Selnau, S. Martinez, P. Kalamegham, A. Tan, G. Campos, M. Veles, J. Zyss, I. Ledoux and L. T. Cheng, *J. Am. Chem. Soc.*, 1995, **117**, 2214.

13 K. A. Bello and J. O. Ajayi, *Dyes Pigm.*, 1996, **31**, 79.

14 M. Adachi and S. Nakamura, *Dyes Pigm.*, 1991, **17**, 287.

15 R. Dworczak, W. M. F. Fabian, B. N. Pawar and H. Junek, *Dyes Pigm.*, 1995, **29**, 65.

16 G. J. Ashwell, G. S. Bahra, C. R. Brown, D. G. Hamilton, C. H. L. Kennard and D. E. Lynch, *J. Mater. Chem.*, 1996, **6**, 23.

17 S. Dibella, G. Lanza, I. Fragala, S. Yitzchaik, M. A. Ratner and T. J. Marks, *J. Am. Chem. Soc.*, 1997, **119**, 3003.

18 R. S. Mulliken, C. A. Reike, D. Orloff and H. Orloff, *J. Chem. Phys.*, 1949, **17**, 1248.

19 C. L. Honeybourne, *J. Mater. Sci.*, 1990, **25**, 3843.

20 D. Pugh and J. O. Morley, in *Nonlinear Optical Properties of Organic Materials and Crystals* (Ed. D. S. Chemla and J. Zyss), Vol. 1, Academic Press, Orlando, 1987, p. 193.

21 G. J. Ashwell, M. P. S. Roberts and N. D. Rees, *Langmuir*, 1998, **14**, 5279.

22 C. Runser, A. Fort, M. Barzoukas, C. Combellas, C. Suba, A. Thiebault, R. Graff and J. P. Kintzinger, *Chem. Phys.*, 1995, **193**, 309.

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