Table I. Activation Energies of Reactions of Hydrated Electrons

Reactant (X)	pH	Relative to e_{aq}^- + NO_3^- (20°) $k_{e_{aq}^-+X}$, M^{-1} sec^{-1}	$\Delta(\Delta E)_{NO_3^-}$, kcal/mole	Relative to e_{aq}^- + PBP (20°) $k_{e_{aq}^-+X}$, M^{-1} sec^{-1}	$\Delta(\Delta E)_{PBP}$, kcal/mole	$\Delta(\Delta E)_{av}$, kcal/mole	$\Delta E_{e_{aq}^-+X}$, kcal/mole	$\Delta S^{\pm}$,[b] cal mole^{-1} deg^{-1}	Specific rate constant (lit.)
H_3O^+	3	4.0×10^{10}	+0.4	2.5×10^{10}	0.0	+0.2	3.2[a]	−2.2	2.36×10^{10}[c]
NO_2^-	5.5–6	..	...	3.4×10^9	0.0	0.0	3.4	−6.2	$3.5–8.1 \times 10^9$,[d]
$[Co(NH_3)_5H_2O]^{+3}$	5.5–6	5.8×10^{10}	0.0	4.6×10^{10}	+0.5	+0.2	3.2	−0.7	$6.1–7.6 \times 10^{10}$ [e]
NO_3^-	5.5–6	..	...	1.1×10^{10}	−0.5	−0.5	3.9	−3.85	$8.2–11 \times 10^9$ [f]
2-Aminopyrimidine	5.5–6	1.4×10^{10}	−0.5	1.3×10^{10}	−0.2	−0.3	3.7	−3.4	..
p-Bromophenol	5.5–6	1.2×10^{10}	+0.4	..	...	+0.4	3.0	−3.7	....
Cyclohexanone	5.5–6	8×10^9	−0.1	7.8×10^9	−0.4	−0.2	3.6	−4.5	....
Phthalate ion	7	4.5×10^9	0.0	4.6×10^9	+0.5	+0.2	3.2	−5.7	6.2×10^9 [g]
Benzoate ion	7	3.6×10^9	−0.4	2.7×10^9	0.0	−0.2	3.6	−6.3	3.1×10^9 [g]
Pyridine	5.5–6	3×10^9	−0.5	4.6×10^9	−0.5	−0.5	3.9	−6.0	$1–3.7 \times 10^9$[h]
Benzenesulfonate ion	7	1.15×10^9	−0.6	8×10^8	+0.4	−0.1	3.5	−8.6	4×10^9 [i]
Chloroacetate ion	7	1.1×10^9	−0.4	..	...	−0.4	3.8	−8.5	$1.2–3.8 \times 10^9$ [j]
Benzyl alcohol	5.5–6	1.9×10^8	−0.1	1.8×10^8	−0.5	−0.3	3.7	−12.0	1.3×10^8 [i]
Phenylalanine	7	1.6×10^8	−0.4	1.35×10^8	+0.3	0.0	3.4	−12.3	$8.8–15 \times 10^7$ [k]
Acetamide	5.5–6	4×10^7	−0.2	3.0×10^7	0.0	−0.1	3.5	−15.1	1.7×10^7 [l]
Formamide	5.5–6	3.8×10^7	+0.2	..	...	+0.2	3.2	−15.25	4.2×10^7 [l]
Phenyl acetate ion	7	3.1×10^7	+0.3	3.3×10^7	−0.4	0.0	3.4	−15.6	$1.4–5.1 \times 10^7$ [g]
Urea	5.5–6	2.7×10^5	0.0	..	...	0.0	3.4	−25.1	3×10^5 [l]

$\Delta(\Delta E)_{NO_3^-} = \Delta E_X - \Delta E_{NO_3^-}$ $\Delta(\Delta E)_{PBP} = \Delta E_X - \Delta E_{PBP}$

[a] We use the value of Thomas, *et al.*,[3] as that of Baxendale, *et al.*,[5] was derived from measurements at two temperatures only. [b] Calculated for ΔE = 3.5 kcal/mole. [c] S. Gordon, E. J. Hart, M. S. Matheson, J. Rabani, and J. K. Thomas, *J. Am. Chem. Soc.*, **85**, 1379 (1963). [d] B. Cercek, private communication, to be published, and ref 5. [e] M. Anbar, E. M. Fielden, and E. J. Hart, unpublished, and ref 5. [f] B. Cercek, private communication, to be published, and ref 3. [g] A. Szutka, J. K. Thomas, S. Gordon, and E. J. Hart, *J. Phys. Chem.*, **69**, 289 (1965). [h] E. J. Hart, S. Gordon, and J. K. Thomas, *J. Phys. Chem.*, **68**, 1271 (1964), and B. Cercek, private communication, to be published. [i] M. Anbar and E. J. Hart, *J. Am. Chem. Soc.*, **86**, 5633 (1964). [j] D. M. Brown, F. S. Dainton, J. P. Keene, and D. C. Walker, *Proc. Chem. Soc.*, 266 (1964); M. Anbar and E. J. Hart, *J. Phys. Chem.*, **69**, 271 (1965). [k] R. Braams, *Radiation Res.*, **27**, 319 (1966). [l] M. Anbar, E. M. Fielden, and E. J. Hart, unpublished

examples for such cases. The higher values of ΔE reported for $e_{aq}^- + Mn^{+2}$ and $e_{aq}^- + Co^{+2}$ reactions in neutral solution are probably due to preequilibria between aquo complexes at different degrees of hydrolysis. It has been shown[10] that the degree of hydrolysis has a significant effect on the rate of reaction of e_{aq}^- with transition metal ions. It remains to be demonstrated that these ions have a lower ΔE in acid solution. Another type of e_{aq}^- reaction which might have $\Delta E > 3.5$ kcal/mole are those which proceed by an atom-transfer mechanism,[11] $e_{aq}^- + X \rightarrow OH^- + HX$. $e_{aq}^- + H_2O$ is the most likely process to take place by this mechanism.

It has been suggested that e_{aq} reactions involve the incorporation of an electron into the orbitals of the substrate;[1] thus their rate depends primarily on the electron distribution of the latter. This distribution, which might be changed by electron excitation, is not expected to be affected by temperature up to 100°. What should therefore determine the rate of e_{aq}^- reactions is the probability of finding an electron vacancy on the substrate molecule; this probability which is represented by the entropy of activation is temperature independent in our range of temperatures. Our findings that $\Delta E^{\pm}$ for all $e_{aq}^- + X \rightarrow X^-$ reactions is equal to the energy of activation of diffusion in water corroborated these conclusions.

Slow $e_{aq}^- + X \rightarrow X^-$ reactions take place with polyatomic reactants only. These reactions involve a large number of collisions with substrate molecules having an unfavorable electronic configuration. An interaction of e_{aq}^- with a reactant molecule in a favorable electronic configuration results in the formation of an activated complex. Once an activated complex has been formed the electron transfer in it is expected to occur within $<10^{-14}$ sec according to the Frank–Condon principle.

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M. Anbar
The Weizmann Institute of Science
Rehovoth, Israel

Z. B. Alfassi, H. Bregman-Reisler
The Soreq Nuclear Research Center
Yavne, Israel

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Conformational Aspects of Polypeptide Structure. XX. Helical Poly-N-methyl-L-alanine. Experimental Results[1]

Sir:

Considerable effort has been expended on the conformational analysis of poly-L-proline in solution.[2–9] Hydrogen bonding is impossible because the amide nitrogens are alkylated. Nevertheless, poly-L-proline can exist in two *ca.* threefold helical forms, poly-L-proline

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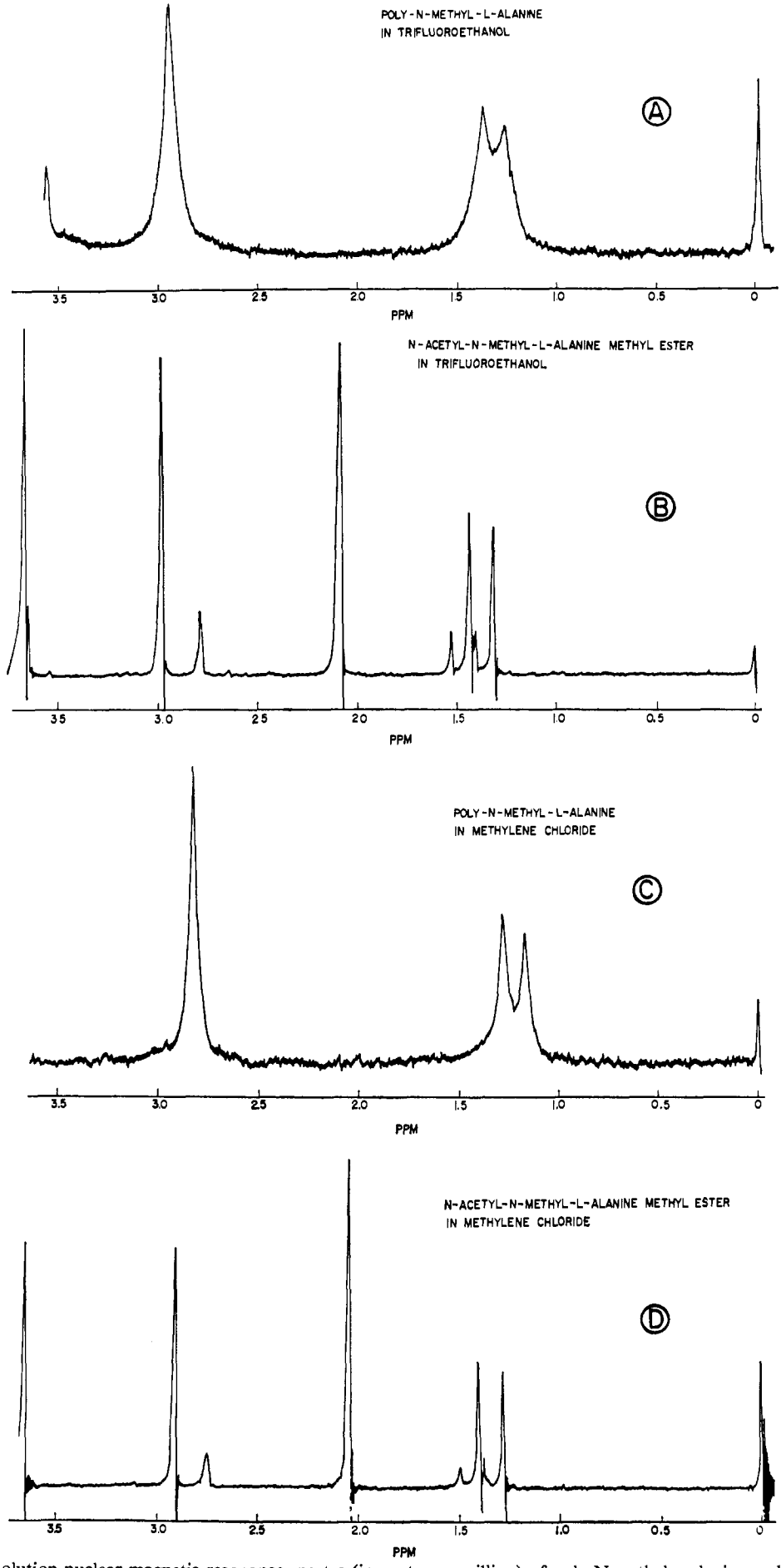

Figure 1. High-resolution nuclear magnetic resonance spectra (in parts per million) of poly-N-methyl-L-alanine and N-acetyl-N-methyl-L-alanine methyl ester in trifluoroethanol and methylene chloride: (A) C–CH_3, doublet, 1.35; N–CH_3, singlet, 3.0 ppm; (B) C–CH_3, two doublets, 1.35 and 1.47; N–CH_3, two singlets, 3.0 and 2.8; (C) C–CH_3, doublet, 1.25; N–CH_3, singlet, 2.8; (D) C–CH_3, two doublets, 1.35 and 1.45; N–CH_3, two singlets, 2.87 and 2.80.

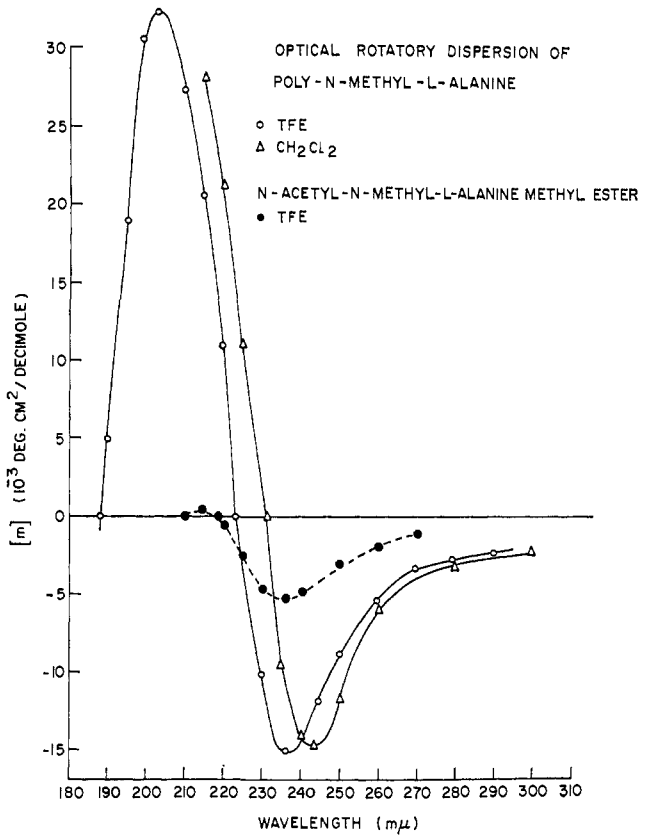

Figure 2. Optical rotatory dispersion of poly-N-methyl-L-alanine and N-acetyl-N-methyl-L-alanine methyl ester in trifluoroethanol and methylene chloride.

We prepared poly-N-methyl-L-alanine, an acyclic analog of poly-L-proline also incapable of hydrogen-bond formation, and found it to be helical on the basis of evidence presented below.[11] Thus the helicity of these N-alkylated polypeptides does not depend on the geometric restrictions imposed by the pyrrolidine ring. The pyrrolidine ring does, however, limit poly-L-proline to one *cis* and one *trans* peptide structure.

We synthesized N-acetyl-N-methyl-L-alanine methyl ester as a model compound for poly-N-methyl-L-alanine. Using high-resolution nuclear magnetic resonance (nmr) we were able to demonstrate the presence of both *cis*- and *trans*-amides for the model compound (Figure 1).[11] Poly-N-methyl-L-alanine, on the other hand, exhibits only *trans*-amide peaks in the solvents studied (Figure 1).[11] These nmr results are consistent with a helical structure for the acyclic polypeptide.

The absorption maximum for the poly-N-methyl-L-alanine lies at 201 mμ (ε 5600) with a shoulder at ~190 mμ (ε 4450). The model compound exhibits a maximum absorption at 196 mμ (ε 7800, uncorrected for the ester group). These results indicate a hypochromism for the polymer and could be explained by the coupling of the transition moments of the neighboring amide groups as in polypeptide α-helices.[12,13]

Optical rotatory dispersion (ORD) (Figure 2) studies on poly-N-methyl-L-alanine in trifluoroethanol (TFE) show a trough at 236 mμ ([m'] −15,000°) with a crossover at 222 mμ and a peak at 202 mμ ([m'] +32,000°). In dioxane and methylene chloride a 6-mμ red shift for these absorption bands is observed. The ORD spec-

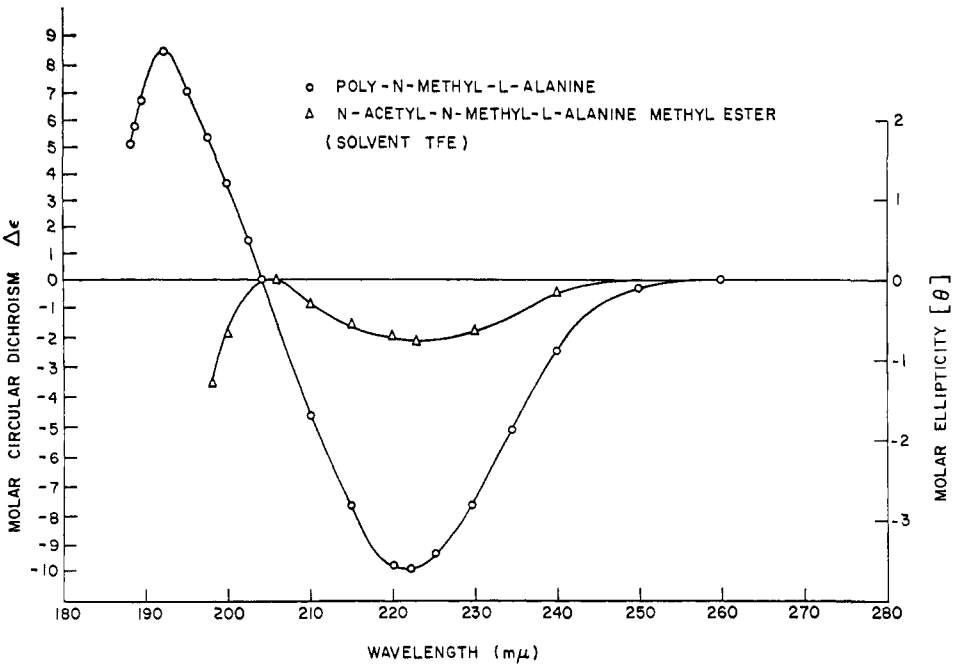

Figure 3. Circular dichroism of poly-N-methyl-L-alanine and N-acetyl-N-methyl-L-alanine methyl ester in trifluoroethanol.

I,[8] a right-handed helix with a residue translation of 1.85 A and with all peptide bonds in the *cis* configuration, and poly-L-proline II,[9] a left-handed helix with a residue translation of 3.12 A and with all peptide bonds in the *trans* configuration. The reversible cooperative transformation between forms I and II has been demonstrated.[10]

trum[14-16] of the model compound (Figure 2) in TFE

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exhibits only a weak version of the trough at 236 mμ ([m'] −4800°).

Circular dichroism data in TFE (Figure 3) show a broad unsymmetrical negative band with a trough at 223 mμ (Δε −10.0). In dioxane and methylene chloride once again we observe that the trough undergoes a red shift to 226 mμ. A second circular dichroism band appears in TFE at 192 mμ (Δε +8.5), with a much smaller area under the curve. We believe that this peak has its origin in a 190-mμ amide $\pi \rightarrow \pi^*$ transition, while the higher wavelength trough is composed of the overlapping of $\pi \rightarrow \pi^*$ and large $n_1 \rightarrow \pi^*$ transitions for the amide group.[14-16] It appears as if a positive band represents the low-wavelength part of a split $\pi \rightarrow \pi^*$ transition. The higher wavelength negative portion falls under the large $n-\pi^*$ band. The circular dichroism of the model compound (Figure 3) shows only the trough at 223 mμ (Δε +1.5), and there does not appear to be a positive $\pi \rightarrow \pi^*$ absorption in the 192-mμ region.

The helical structure of poly-L-proline II as noted above was clearly established by X-ray diffraction analysis.[9] In spite of the fact that it is a left-handed helix, this polymer exhibits negative optical rotatory dispersion and circular dichroism peaks.[6,7] We obtained similar spectral results for poly-N-methyl-L-alanine; our results do differ somewhat from those obtained with poly-L-proline in that no *cis* form has been detected.

The α-amino acid N-carboxyanhydride (NCA) of N-methyl-L-alanine was prepared from alanine by the method of Quitt, Hellerbach, and Vogel.[17] The NCA was then polymerized by benzylamine initiation in anhydrous dioxane over a period of 2–3 weeks to obtain high molecular weight poly-N-methyl-L-alanine (mp 280–290°) in high yield.

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Murray Goodman, Maria Fried
Department of Chemistry, Polytechnic Institute of Brooklyn
Brooklyn, New York
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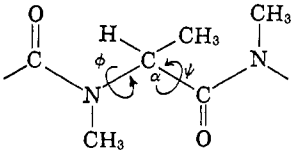
Conformational Aspects of Polypeptide Structure. XXI. Helical Poly-N-methyl-L-alanine. Theoretical Results

Sir:

In the preceding paper[1] compelling evidence in support of a helical conformation for poly-N-methyl-L-alanine was presented. In the present study stable helical forms of this peptide chain are determined by calculations of conformational energies using well-established methods.[2-5] Since it has been amply demonstrated that steric interactions are of predominant importance in the determination of allowed conformations of chain molecules,[5,6] the preliminary calculations described here include only this type of nonbonded interaction.[7] Additionally, it is assumed that all of the amide bonds in the poly-N-methyl-L-alanine chain are *trans*, and that rotational angles about N–CH_3 and C_α–CH_3 bonds are fixed and thus do not enter as variables in the conformational energy calculation. The torsional energy contribution for rotations about N–C_α and C_α–CO skeletal bonds was calculated assuming potential minima at 0 and ±120° with barrier heights of 1.5 and 1.0 kcal mole^{-1}, respectively, at ±60 and 180°.[8] van der Waals interactions between all pairs of nonbonded atoms in the dipeptide sequence



were estimated using standard bond angles and bond lengths[4] and Lennard-Jones "6–12" potential functions.[4] The sum of the torsional and van der Waals interaction energies, taken to be the conformational energy E, was plotted as a function of the rotation angles φ about N–C_α and ψ about C_α–CO bonds in the customary manner.[9] Both angles were varied from 0 to 360° in 10° increments.

The most striking feature of the resulting contour map[10] of the conformational energy is that regions representing 5 kcal mole^{-1} or less of energy make up only approximately 2.5% of the total topographical area. Since only these regions are accessible to the chain at normal temperatures, the poly-N-methyl-L-alanine chain is seen to be extremely restricted in the number of conformations it can assume. Four minima in the energy were found, and are described in Table I.

Table I. Low-Energy Conformations of the Poly-N-methyl-L-alanine Chain

Helix	φ, deg	ψ, deg	E, kcal mole^{-1}
I	30	250	−0.85
II	210	250	−0.33
III	80	345	2.54
IV	240	345	1.50

Of immediate interest is the fact that the right-handed α-helix ($\varphi = 132°$, $\psi = 123°$),[9,11] a stable conformation for poly-L-alanine,[4,8] does *not* represent a low-energy form for poly-N-methyl-L-alanine. This is a result of severe steric repulsion between α-methyl and N-methyl groups in this conformation of the N-substituted chain.

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