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Molecular and Internal Reorientation in 1,1,2,2-Tetraphenylethane

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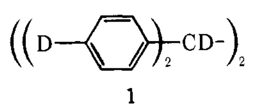
Abstract: Deuterium spin-lattice relaxation time (T_1) data for 1,1,2,2-tetra(phenyl-*4-d*)ethane-*1,2-d*$_2$ and 1,1,2,2-tetra(phenyl-*2,6-d*$_2$)ethane-*1,2-d*$_2$ have been employed to determine the relative rates of internal and molecular reorientation. The rate ratio varies from ca. 0.7 to 2.0 over the temperature range 300–340 K, indicating that the two processes are commensurate in rate.

The conformational analysis of 1,1,2,2-tetraphenylethane (TPE) has proven to be of exceptional interest. It was originally predicted by empirical force field (EFF) calculations that TPE prefers an H–H anti conformation by ca. 5 kcal/mol over any gauche conformation.[2] This prediction was subsequently verified[3] by the observation that the vicinal (ethano) coupling constant ($^3J_{HH}$) has a value of 11.3 Hz and that the X-ray structure of TPE is remarkably similar to that predicted by the EFF calculations. It is noteworthy that in contrast to TPE and other unclamped tetraarylethanes,[4] 1,1,2,2-tetraalkylethanes prefer the gauche conformation.[5]

The static stereochemistry of TPE and its derivatives thus being thoroughly established, a secure basis is provided for any study aimed at an understanding of the dynamic stereochemistry of this system. In a previous paper on the conformational dynamics of 1,1,2,2-tetraarylethanes,[6] we reported an analysis of internal aryl ring rotations based on DNMR spectroscopy. To complete the description of these dynamic processes, it was desirable to obtain information relative to molecular as well as internal modes of reorientation. TPE possesses a sufficient number of heterotopic nuclei so that a unique description of its motion can be obtained within the framework of existing relaxation theory. Relaxation theories for dipolar and quadrupolar nuclei have been presented for molecules undergoing rigid isotropic reorientation, isotropic reorientation with internal motion, rigid anisotropic reorientation, and anisotropic reorientation with internal motion.[7-17] The present study reports an application of Woessner's theory of anisotropic reorientation with concomitant internal reorientation.[8,17]

Results

Two specifically deuterated derivatives of TPE, 1,1,2,2-tetra(phenyl-*4-d*)ethane-*1,2-d*$_2$ (**1**) and 1,1,2,2-tetra(phenyl-*2,6-d*$_2$)ethane-*1,2-d*$_2$ (**2**), were synthesized by standard methods for a study of the requisite relaxation times. A study of the molecule containing the combined substitution patterns of **1** and **2**, i.e., 1,1,2,2-tetra(phenyl-*2,4,6-d*$_3$)ethane-*1,2-d*$_2$, was precluded by the fact that the aromatic resonances in TPE (^{1}H) and in **1** and **2** (^{2}H) are accidentally isochronous.



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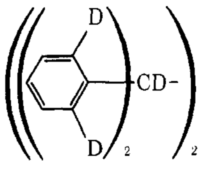

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Deuteron relaxation times were determined by the standard inversion-recovery technique.[18] The results are presented in Table I. Correlation times were calculated employing the formula

$$T_1^{-1} = \tfrac{3}{2}\pi^2(Q_D)^2\tau_c$$

where T_1 is the experimental spin-lattice relaxation time, τ_c is the correlation time, and Q_D is the quadrupole coupling constant.[19] The values of Q_D employed in the calculations were 160 kHz for the ethano bridge (br) deuterons and 210 kHz for the aromatic ortho (o) and para (p) deuterons.[20]

Over the temperature range studied (300–340 K), τ_{br} values for **1** and **2** are, as expected, equal within experimental error, thus allowing a valid comparison of τ_o and τ_p at corresponding temperatures. Least-squares analysis of the temperature dependence of τ_{br}, τ_o, and τ_p yielded energies of activation of 4.05 ± 0.62, 3.90 ± 0.29, and 2.90 ± 0.48 kcal/mol for the bridge, ortho, and para deuterons, respectively, at the 95% confidence level.

Discussion

The present results demonstrate that it is possible to employ existing relaxation theories to describe the reorientation of complex molecules, such as TPE. The unequal correlation times and energies of activation for correlation times of the bridge and para deuterons indicate anisotropic reorientation for **1** and **2**; if reorientation were isotropic, these two deuterons, in the absence of central bond rotation (see below), would necessarily exhibit equal correlation times and energies of activation.[25] In order to ascertain whether anisotropic reorientation alone suffices to account for the ratios of observed correlation times for **1** and **2**, the following analysis was undertaken.

As a first step, it was necessary to develop a model for the overall shape of TPE which would be amenable to treatment by the existing theories of molecular reorientation. Only anti conformations of **1** and **2** were considered, since the most stable calculated anti conformer of TPE is ca. 5 kcal/mol lower in energy than the most stable gauche conformer;[2] the population of the latter is therefore expected to be negligible under the present conditions of measurement.[26] By the same token, since the minimum activation energy for anti → gauche interconversion is presumed to be significantly greater than that of the reorientation process, we do not expect the rate of central C–C bond reorientation (rotation) to be commensurate with molecular reorientation. The dimensions of the *anti*-TPE molecule in the inertial coordinate system (Figure 1) were calculated from the following intramolecular separations. The distance between the two para deuterons on geminal phenyl rings ($r_{D_1D_2}$), the distances between the two para deuterons on the vicinal aryl rings (cis ($r_{D_1D_3}$) and trans ($r_{D_2D_3}$)), and the projection onto the z axis of the line joining the meta protons H_m and H'_m (in the perpendicular conformation; see Table II,

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Table I. ^{2}H Relaxation and Correlation Times of **1** and **2**

temp, K	compd	deuteron	T_1 s[a]	τ_c, ps[b]	τ ratios br/p	τ ratios o/p
300	**1**	bridge	0.075 ± 0.005	35.2	1.40	
		para	0.061 ± 0.003	25.1		
	2	bridge	0.074 ± 0.008	35.7		0.69
		ortho	0.088 ± 0.006	17.4		
320	**1**	bridge	0.115 ± 0.006	22.9	1.20	
		para	0.080 ± 0.015	19.1		
	2	bridge	0.118 ± 0.011	22.4		0.59
		ortho	0.136 ± 0.002	11.3		
340	**1**	bridge	0.162 ± 0.018	16.3	1.14	
		para	0.107 ± 0.013	14.3		
	2	bridge	0.165 ± 0.009	16.0		0.56
		ortho	0.190 ± 0.011	8.06		

[a] Average of a minimum of three separate determinations. [b] Calculated from $T_1^{-1} = \frac{3}{8}(e^2Q_q/\hbar^2)^2\tau_c$; $(e^2Q_q/h) = Q_D$ (Q_D(aryl) = 210 kHz; Q_D(alkyl) = 160 kHz).

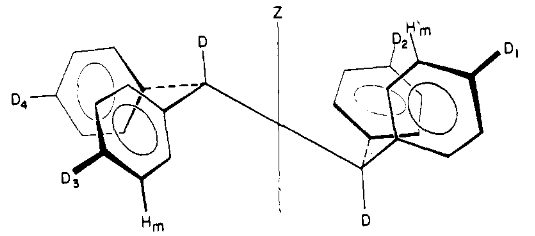

Figure 1. Schematic of the inertial coordinate system. The origin is at the center of the ethane C–C bond. The x axis is perpendicular to the plane of the paper.

footnote e) approximate the molecular width (ca. 9.3 Å), length (ca. 7.1 Å), diameter (11.6 Å), and height (ca. 4.5 Å), respectively. The molecular shape of TPE is therefore roughly approximated by an axially symmetric ellipsoid and, as such, the relaxation data can be treated employing the Woessner equation.[8,17]

The principal moments of inertia of the various conformations were computed from molecular geometries generated by EFF calculations[2] and from certain idealized geometries. Initially, diffusion coefficients (D_i) were assumed to be inversely proportional to the square roots of the corresponding moments of inertia,[27] and the direction cosines of the pertinent (br, o, and p) C–D bonds with respect to the principal axes of inertia were computed. The moments of inertia and relative diffusion coefficients are presented in Table II. It should be noted that for all conformations, $I_{xx} \approx I_{yy} \approx 2I_{zz}$, as for a planar symmetric top; however, this model does not fit TPE since the experimental relaxation data are inconsistent with the calculated moments of inertia (see below).

From these data the ratios of nuclear correlation times were obtained by use of the Woessner equation.[8] The results are presented in Table II for the two deuterons unaffected by internal (aryl) reorientation, i.e., for the deuterons on the ethano bridge (br) and in the para position (p). The ratios were calculated on the assumption, which has been successfully employed before in other cases,[31-34] that the inertial and correlational axes are coextensive.

Whereas experimental values of τ_{br}/τ_p vary with temperature from 1.40 to 1.14 (Table I), the calculated ratio for all anti conformations of **1** is ca. 0.87 (Table II). A possible explanation for the discrepancy between observed and calculated values could be a breakdown in the assumption that the diffusion and inertial axes are coextensive. However, rotation of the central C–C bond about the x axis into the y axis (Figure 1) does not lead to substantial improvement in the computed values; when the central bond is coincident with the inertial y axis, $\tau_{br}/\tau_p = 0.93$. It is clear that on reorientation about the inertial coordinate system, no single conformation of TPE is capable of reproducing the experimental ratio.

In order to reproduce the observed ratios it is therefore necessary to adjust the diffusion coefficients. Variation of D_x and/or D_y does not markedly alter τ_{br}/τ_p, but adjustment of D_z (while equating D_x and D_y, since I_{xx} and I_{yy} are nearly equal) results in excellent agreement between calculated and experimental values (Table III). The necessity of altering D_z appears reasonable; enhanced reorientation about the z axis should be favored since solvent displacement during reorientation is less about this axis than about any other. Similarly, benzene, at temperatures well below its boiling point, is known to reorient more rapidly about its C_6 symmetry axis than about any axis coincident with the molecular plane, presumably because solvent displacement is least for this in-plane motion.[35]

Comparison of the experimental values for τ_o/τ_p with those calculated for the EFF conformation (Table III) reveals substantial discrepancies. However, by employing the Woessner equation for anisotropic reorientation[17] with concomitant internal reorientation, total agreement between experimental and calculated τ_{br}/τ_p and τ_o/τ_p ratios is obtained with reasonable values for the internal diffusion coefficient (D_i).[36]

The data in Table III can be interpreted in the qualitative sense that as the temperature increases, molecular reorientation becomes less anisotropic (the ratio D_z/D_j, $j = x$ or y, decreases) and internal reorientation increases (D_i increases). It can be concluded from the values of the rate ratios that internal reorientation is commensurate in rate with molecular reorientation; we note that in previous cases internal reorientations have either been assumed[33] or have been demonstrated[31] to be slow relative to overall molecular reorientation. A more quantitative interpretation of our results is precluded, principally because the Woessner equation requires that all internal rotational angles be populated with equal probability. This condition is certainly not fulfilled in the case of TPE.[37]

It remains to be noted that additional support can be mustered for our conclusion that TPE approaches more isotropic reorientation with increasing temperature, as judged by the decrease in D_z. If TPE were isotropically reorienting, exact values for D_i would be obtainable.[8,9] For an isotropically reorienting molecule with a single internal reorientation:

$$\tau_c = \frac{\frac{3}{4}\sin^4\Delta}{6D_{iso} + 4D_i} + \frac{3\sin^2\Delta\cos^2\Delta}{6D_{iso} + D_i} + \frac{[\frac{1}{2}(3\cos^2\Delta - 1)]^2}{6D_{iso}}$$

where Δ is the angle subtended by the rotating bond and the rotation axis, D_{iso} is the isotropic rotational diffusion coefficient, and D_i is the internal diffusion coefficient. In TPE, $\Delta = 60°$ for the ortho and 0° for the para C–D bond. Thus,

Table II. Moments of Inertia, Relative Diffusion Coefficients, and Correlation Ratios for **1**

	moments of inertia, amu Å^2			rel diffusion coeff[b]			calcd[c]
conformation[a]	I_{xx}	I_{yy}	I_{zz}	D_x	D_y	D_z	τ_{br}/τ_p
EFF[d]	2035	2551	3876	1.0	0.89	0.72	0.874
perpendicular[e]	1958	2275	3870	1.0	0.93	0.71	0.874
planar[f]	2002	2237	3864	1.0	0.95	0.72	0.872
all rings 60° [g]	1978	2299	3827	1.0	0.93	0.72	0.879

[a] All anti (dihedral angle HCCH = 180°). [b] $D_i = (I_{ii}/I_{xx})^{-1/2}$. [c] Calculated employing eq 41 of ref 8 modified for quadrupolar relaxation. [d] Calculated ground-state conformation (ref 2). [e] All dihedral angles between plane defined by (C_1, C_2, C_{aryl}) and the planes defined by the aryl rings equal 90°. [f] All dihedral angles between plane defined by (C_1, C_2, C_{aryl}) and the planes defined by the aryl rings equal 0°. [g] All dihedral angles between plane defined by (C_1, C_2, C_{aryl}) and the planes defined by the aryl rings equal 60°.

Table III. Correlation Time Ratios

	τ_{br}/τ_p			τ_o/τ_p				
temp, K	exptl	calcd[a]	calcd[b]	exptl	calcd[a]	calcd.[b]	D_z[c]	D_i[d]
300	1.40	1.40	1.41	0.69	1.26	0.69	2.10	1.50
320	1.20	1.20	1.21	0.59	1.14	0.60	1.50	2.50
340	1.14	1.14	1.15	0.56	1.10	0.57	1.35	2.75

[a] Calculated employing the Woessner equation for anisotropic rigid reorientation.[8] [b] Calculated ratio employing the Woessner equation for combined anisotropic and internal reorientation.[17] [c] $D_x = D_y = 1.0$. [d] Internal diffusion coefficient.

$$\frac{1}{6D_{iso}}\left[\left(\frac{\tau_o}{\tau_p}\right)_{exptl}\right] = \frac{\frac{3}{4}\sin^4 60}{6+4D_i} + \frac{3\sin^2 60\cos^2 60}{6+D_i} + \frac{[(\frac{1}{2}(3\cos^2 60 - 1)]^2}{6}$$

For TPE at 300, 320, and 340°, respectively, the approximate D_i/D_{iso} ratios are 1.40, 2.29, and 2.63, respectively. The more exact treatment (Table III) yields D_i = 1.50, 2.50, and 2.75, respectively, at the corresponding temperatures. Thus, the isotropic approximation yields reasonable estimates of internal reorientation rates.[39]

Experimental Section

Melting points were taken with a Thomas-Hoover melting point apparatus and are corrected. Proton nuclear magnetic resonance spectra were recorded on a Varian A-60 instrument using $CDCl_3$ solution with internal Me_4Si as reference. Relaxation time measurements were performed on saturated solutions of **1** and **2** in purified cyclohexane (ca. 7 mg/mL) employing the standard inversion-recovery pulse sequence with a Bruker HX-90 spectrometer operating at 13.82 MHz. A total of 500 transients containing 4K of data points were acquired for each spectrum with a spectral width of 500 Hz. Operating with a single-coil configuration, the 90° pulse width was 15 μs. The samples were confined to the RF coil in 10-mm cylindrical cells. The temperature of the sample probe was regulated to within ±0.2 °C. The spectrometer was locked on the proton resonance of cyclohexane. For each sample, three to nine repeat measurements were made at the same temperature.

Bromobenzene-*2,6-d*$_2$. Benzoic-*2,6-d*$_2$ acid[40] (8.0 g, 64.5 mmol) was dissolved in a solution of NaOH (2.6 g, 64.5 mmol) in 200 mL of water. The pH was adjusted (with HNO_3) until the solution was slightly acidic. A solution of $AgNO_3$ (12.0 g, 70.6 mmol) in 15 mL of H_2O was added and the resulting flocculent white precipitate was collected and dried at 80 °C under vacuum. The silver benzoate-*2,6-d*$_2$ ((11.8 g, 51.1 mmol) was refluxed in 100 mL of CCl_4, and bromine (8.5 g, 53.2 mmol) in 20 mL of CCl_4 was added. After 2 h of reflux, the reaction mixture was filtered while hot and the filtrate was washed successively with aqueous $NaHSO_3$ and $NaHCO_3$ solutions. Distillation yielded bromobenzene-*2,6-d*$_2$ (2.0 g, 20%). The NMR spectrum consisted of a broad singlet at δ 6.98 (strikingly different from the complex pattern observed for undeuterated bromobenzene).

Benzhydrol-*4,4′-d*$_2$. A Grignard reagent was prepared from bromobenzene-*4-d*[41] (3.5 g, 22.2 mmol) and reacted with ethyl formate (0.89 mL, 11.1 mmol) in 4 mL of ether. The usual workup with saturated NH_4Cl solution, drying with Na_2SO_4, and recrystallization from 30-60 °C benzin yielded benzhydrol-*4,4′-d*$_2$ (1.0 g, 51%), mp 64-66 °C. The NMR spectrum consisted of signals at δ 7.35 (s, 8 H), δ 5.83 (s, 1 H), and a broad singlet at δ 2.08 (1 H). The mass spectrum showed a parent peak at *m/e* 186 (184 for unlabeled benzhydrol), and indicated that the undeuterated material constituted at most 5% of the sample.

Benzhydrol-*2,2′,6,6′-d*$_4$ was prepared in the same manner as the preceding compound from bromobenzene-*2,6-d*$_2$. The NMR spectrum consisted of signals at δ 7.25 (s, 6 H), δ 5.74 (s, 1 H), and δ 2.40 (s, 1 H).

Benzophenone-*4,4′-d*$_2$. A solution of benzhydrol-*4,4′-d*$_2$ (1.1 g, 5.9 mmol) in 10 mL of CH_2Cl_2 was added to a sixfold excess of chromium trioxide-pyridine complex in 100 mL of CH_2Cl_2.[42] A gummy brown solid precipitated immediately. The reaction mixture was stirred for 15 min. Decanting the solution, washing it in succession with aqueous solutions of 5% NaOH, 5% HCl, 5% $NaHCO_3$, and saturated NaCl, and drying over Na_2SO_4 followed by removal of solvent under reduced pressure gave benzophenone-*4,4′-d*$_2$ (1.1 g, 100%) as a thick oil. The NMR spectrum of the AA′BB′ spin system appeared as an AB quartet with a doublet centered at δ 7.76 and another at δ 7.46, with an apparent J_{AB} of 7.6 Hz.

Benzophenone-*2,2′,6,6′-d*$_4$ was prepared in the same manner as the preceding compound from benzhydrol-*2,2′,6,6′-d*$_4$. The NMR spectrum consisted of two broad singlets at δ 7.45 and 7.26.

Di(phenyl-*4-d*)carbinol-*1-d*. A solution of benzophenone-*4,4′-d*$_2$ (1.13 g, 6.13 mmol) in 10 mL of ether was added to a slurry of $LiAlD_4$ (0.26 g, 6.13 mmol, Stohler, 99%D) in 10 mL of ether. After stirring overnight, quenching with aqueous saturated NH_4Cl solution, and routine workup, di(phenyl-*4-d*)carbinol-*1-d* (1.0 g, 88%) was obtained as a white solid, mp 63-65 °C. The NMR spectrum showed no methine signal.

Di(phenyl-*2,6-d*$_2$)carbinol-*1-d* was prepared in the same manner as the preceding compound from benzophenone-*2,2′,6,6′-d*$_4$. The NMR spectrum showed no methine signal.

1,1,2,2-Tetra(phenyl-*4-d*)ethane-*1,2-d*$_2$ (1). A deoxygenated solution of di(phenyl-4-*d*)carbinol-1-*d* (1.0 g, 5.4 mmol) in 50 mL of acetone was treated with 20 mL of concentrated HCl and a 15% molar excess of $CrSO_4$ solution.[43] The reaction mixture was poured into 75 mL of water and the white precipitate was filtered and recrystallized from acetone/30-60 °C benzin, yielding **1** (0.40 g, 44%), mp 205-209 °C. The ^{1}H-NMR spectrum consisted of a singlet at δ 7.14. No methine signal was observed. The ^{2}H-NMR spectrum showed two signals with relative integrated intensities of ca. 2:1.

1,1,2,2-Tetra(phenyl-*2,6-d*$_2$)ethane-*1,2-d*$_2$ (2). This compound was prepared in a similar manner as **1** from di(phenyl-*2,6-d*$_2$)carbinol-*1-d*. The ^{1}H-NMR spectrum consisted of a singlet at δ 7.11. The ^{2}H-NMR spectrum showed two signals with relative integrated intensities of ca. 4:1.

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(20) Quadrupole coupling constants observed for deuterons in a number of sp^3 hybridized systems are ca. 160 kHz. For example: CDH$_2$OH, $Q_D = 158.9 \pm 2.9$ kHz;[21] CDH$_2$CN, $Q_D = 156.1 \pm 3.0$ kHz;[21] CDH$_2$I, $Q_D = 163.1 \pm 3.8$ kHz.[22] Those for deuterons in sp^2 hybridized systems are ca. 210 kHz, e.g., C$_6$D$_6$, $Q_D = 196.5 \pm 1.3$ kHz;[23] C$_6$H$_5$D, $Q_D = 207.0 \pm 1.9$ kHz.[24]
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(25) For an isotropically reorienting molecule a single rotational diffusion coefficient (D_{iso}) suffices to describe the molecular reorientation. The correlation time is defined as $\tau_{iso} = (6D_{iso})^{-1}$.
(26) Variable temperature studies[3] of $^3J_{HH}$ (the vicinal ethano coupling constant) indicate that this coupling is invariant with temperature over the range 310–370 K in toluene. This observation rules out an appreciable population of the gauche conformer over the experimental temperature range reported here; otherwise, the magnitude of $^3J_{HH}$ would be expected to decrease with increasing temperature.
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(39) Baldo et al.[30] have recently employed this approximation in treating internal rotation in the diphenyl dichalconides (PhX–XPh; X = S, Se, Te). For these molecules, τ_o/τ_p equals 1.28, 1.84, and 2.04, respectively. It should be noted that two of the D_i/D_{iso} ratios given in Table IV of ref 30 are incorrect; the values given for (PhSe)$_2$ and (PhTe)$_2$ should be 2.84 and 3.65, respectively, rather than 1.74 and 2.18.
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Equilibria Involving Cation Radical Ion Pairs

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Abstract: The equilibrium constants for the dissociation of cation radical ion pairs of 1,2,4,5-tetramethoxybenzene, phenothiazine, and 1,4-dimethoxyanthracene with I_3^- have been measured at −20 °C [$K_d = (1.54 \pm 0.16) \times 10^{-2}$, $(9.7 \pm 2.0) \times 10^{-2}$, and $(4.08 \pm 1.17) \times 10^{-1}$, respectively]. The equilibrium constants were measured by following the changes in g value on addition of varying amounts of I_3^- to solutions of the free radical.

Ever since the first EPR investigations of ion pairs by Adam and Weissman[1] and Atherton and Weissman[2] a great deal of data concerning the structure and thermodynamic parameters controlling the dissociation of organic anion radical ion pairs has appeared in the literature. Four different EPR techniques have been used to determine the ion pair dissociation constants. These include the use of (1) coupling constants,[3-5] (2) line widths (relaxation times),[6] (3) line intensities (spin concentrations),[7-9] (4) g values.[10] Of these, the use of g values has proved to be the most accurate method. The method consists basically of the ability to observe a smooth change in the g value of a radical as a function of counterion concentration and requires the generation of the "free" radical when the concentration of the counterion is zero. The use of EPR g values for the determination of equilibrium constants has also been demonstrated for solvent exchange equilibria.[11]

To date, similar information for cation radical ion pairs has not been available owing to the limited experimental observation of such species.[12-15] Romans et al.[12] first reported a g shift as a function of solvent for the tetramethylhydrazine cation radical produced by iodine oxidation which they at-

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