Conformational equilibrium and normal coordinate analyses of ketenecarboxylic acid O=C=CH–COOH

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Abstract

*The conformational and structural stability of ketenecarboxylic acid O=C=CH-COOH were investigated by DFT-B3LYP and ab initio MP2 calculations with the 6-311+G** basis set. From the calculations ketenecarboxylic acid was predicted to exist predominantly in a mixture of cis (the CO and the CHCO groups eclipse each other) and trans conformations with the trans being the lower energy form. The C-C- and C-O rotational barriers in the molecule were calculated to be about 10 and 12 kcal/mol, respectively. The equilibrium constant for the cis ↔ trans conformational interconversion of ketenecarboxylic acid was calculated to be 0.4117 that corresponds to an equilibrium mixture of about 29% cis and 71% trans at 298.15 K. The vibrational frequencies of the molecule in the cis and trans conformations were computed at the DFT-B3LYP level. Complete vibrational assignments were made on the basis of normal coordinate analyses of cis and trans ketenecarboxylic acid.*

Keywords: Conformational stability; Vibrational spectra and assignments; ketenecarboxylic acid

Résumé

*Nous avons étudié la stabilité conformationnelle et structurelle de l'acide cétènecarboxylique O=C=CH-COOH grâce à DFT-B3LYP et aux calculs ab initio MP2 et la base 6-311+G**. Les calculs prédisent que l'acide cétènecarboxylique existe de façon prédominante dans un mélange de conformations cis (les groupes CO et CHCO s'éclipsant l'un l'autre) et trans, cette dernière forme étant de plus faible énergie. On prédit que les deux conformations possèdent une stabilité relative comparable avec des barrières rotationnelles C-C et C-O d'environ 10 et 12 kcal/mol, respectivement. La constante d'équilibre de l'inter conversion conformationnelle cis ↔ trans de l'acide cétènecarboxylique a été estimée à 0.4117, ce qui correspond à un mélange à l'équilibre d'environ 29% cis et 71% trans à 298.15 K. Les fréquences vibrationnelles de la molécule dans les conformations cis et trans ont été calculées au niveau DFT-B3LYP. L'attribution complète des vibrations a été réalisée sur la base des analyses de coordonnées normales de l'acide cétènecarboxylique cis et trans.*

Introduction

The role of formyl and vinyl ketenes in synthetic and polymer chemistry and their structure were the subject of many studies (1-11). Recently the conformational behavior of formyl ketene CHO-CHCO (12) and vinyl ketene CH_2=CH-CHCO (13) were investigated by DFT and *ab initio* MP2 methods. The two molecules were predicted to exist only in the planar *cis* and *trans* conformations as a result of pronounced conjugation effects, where the non-planar *gauche* structures being transition states.

The relative stability and the size of the rotational barrier in these molecules were predicted to be significantly dependent on the type of substituent. The molecules were predicted to have a high *cis* to *trans* rotational barrier that was attributed to the partial π-character of the C-C bond in the molecules (12 and 13). The C-C rotational barrier was calculated to be about 12 kcal/mol in formyl ketene (12) as compared to 6 kcal/mol in vinyl ketene (13). The *cis* and *trans* conformers of formyl ketene (12) were predicted to have a comparable relative stability. For vinyl ketene the *trans* conformer was predicted to be about 2 kcal/mol lower in energy than the *cis* form (13).

As a continuation of the interest in ketenes, the structure of the corrsponding acid, ketenecarboxylic acid

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CHCO-COOH was investigated by the DFT-B3LYP and *ab initio* MP2 calculations in this study. The energies of the molecule in its possible structures were optimized at both levels of calculations using 6-311+G** basis set. The vibrational frequencies were computed at the DFT-B3LYP level and normal coordinate analyses were then carried out. The potential energy distributions (PEDs) among symmetry coordinates of each normal mode for the stable conformers of the molecule were then calculated. The vibrational assignments of the normal modes were made on the basis of the calculated PED values. The results of the work are presented herein.

Ab inito calculations

The GAUSSIAN 98 program (14), running on an IBM RS/6000 43P model 260 workstation, was used to carry out the DFT-B3LYP and *ab initio* MP2 calculations. The 6-311+G** basis set was used to optimize the structures and to predict the energies and dipole moments of ketenecarboxylic acid in its possible structures (Figure 1). The optimized structural parameters and energies of the molecule at DFT-B3LYP/6-311+G** and MP2/6-311+G** levels are given in Tables 1 and 2.

Asymmetric torsional potential functions

The potential scans for the internal rotations about the C-C and the C-O single bonds were obtained by allowing the CCCO and OCOH dihedral angles (ϕ) to vary from 0º (the *cis* position) to 180º (the *trans* position) in the molecule. Full geometry optimizations at fixed dihedral angles between 0 and 180 with an increment of 15 degrees were carried out at the DFT-B3LYP/6-311+G** and MP2/6-311+G** levels of calculation. Each torsional potential was represented as a Fourier cosine series in the dihedral angle (φ): $V(\varphi) = V_0 + \sum(V_n/2)[1-\cos(n\varphi)]$, where V_0 is the relative energy of the *cis* (CCCO and OCOH dihedral angles are 0º) conformation and the

Table 1. Structural Parameters (Å and degrees), total dipole moment (Debye), and rotational constants of the *cis* and *trans* conformers of ketenecarboxylic acid.

Parameter	B3LYP/6-311+G**		MP2/6-311+G**	
	cis	***trans***	***cis***	***trans***
r (C_1=C_2)	1.325	1.324	1.335	1.335
r (C_2-C_3)	1.460	1.460	1.460	1.459
r (C_3=O_4)	1.210	1.206	1.215	1.214
r (C_3-O_5)	1.358	1.363	1.359	1.366
r (C_1=O_6)	1.151	1.152	1.159	1.160
r (C_2=H7)	1.081	1.081	1.081	1.081
r (O_5-H_8)	0.969	0.968	0.968	0.967
Bond angle				
($C_1C_2C_3$)	119.8	122.1	117.7	120.8
($C_2C_3O_4$)	126.4	125.0	126.2	125.2
($C_2C_3O_5$)	110.6	112.1	110.6	111.6
($C_2C_1O_6$)	179.1	179.2	179.8	179.6
($C_1C_2H_7$)	118.3	118.7	119.1	119.1
($C_3O_5H_8$)	106.7	107.2	105.4	105.8
($C_1C_2C_3O_4$)	0.0	180.0	0.0	180.0
($H_8O_5C_3O_4$)	0.0	0.0	0.0	0.0
Dipole moment (μ_t)				
	2.28	1.05	2.60	1.11
Rotational constants				
A	11011	10642	10895	10622
B	2214	2316	2238	2325
C	1843	1902	1857	1908

Table 2. Computed total energies E (hartree) and relative energies ΔE (kcal/mol) for the *cis* and *trans* conformations and transition state (TS) of ketenecarboxylic acid.

Structure[a]	(φ)	**B3LYP/6-311+G****		(φ)	**MP2/6-311+G****	
		E	**ΔE**		**E**	**ΔE**
cis	(0.0)	-341.290062	0.520	(0.0)	-340.433790	0.271
trans	(180.0)	-341.290891	0.000	(180.0)	-340.434222	0.000
TS	(89.7)	-341.272895	11.293	(90.1)	-340.416828	10.915

[a] ϕ is the optimized CCCO torsional angle.

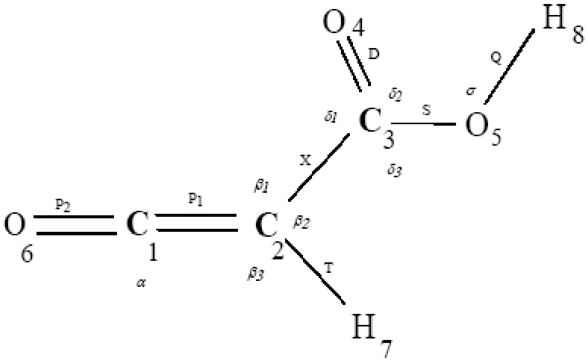

Figure 1. Atom numbering and internal coordinates defintion of ketenecarboxylic acid in the *cis* conformation.

potential coefficients from V_1 to V_6 are considered adequate to describe the potential function. The results of the energy optimization were used to calculate the six coefficients by least-squares fitting (Table 3). The potential functional scans of ketenecarboxylic acid are shown in Figure 2.

Vibrational Frequencies and Normal Coordinate Analyses

The optimized structural parameters of ketenecarboxylic acid were used to calculate the vibrational frequencies of the stable *trans* and *cis* forms at the DFT-B3LYP/6-311+G** level of calculation. Ketenecarboxylic acid in its *trans* and *cis* structures has the C_s symmetry. For ketenecarboxylic acid the 18 vibrational modes span the irreducible representations: 13 A' and 5 A". The A' modes should be polarized whereas the A" modes be depolarized in the Raman spectra of the liquid. Normal coordinate analyses were carried out for the stable conformers of the molecules as described previously (15, 16). The symmetry coordinates of ketenecarboxylic acid are listed in Tables 4. The potential energy distributions (PEDs) among the symmetry coordinates of each normal mode of ketenecarboxylic acid in the *trans* and *cis* conformations were calculated and given in Tables 5 and 6. A reliable assignment of the fundamentals was proposed based on the calculated PED values, infrared band intensities, Raman line activities, and depolarization ratios and experimental data of chlorocarbonyl ketene (19) . The data of the vibrational assignments are listed in Tables 5 and 6.

Table 3. Calculated potential constants (kcal/mol) for the asymmetric OCOH (C-O) and CCCO (C=O) torsions in ketenecarboxylic acid.

Potential constants	**DFT-B3LYP/6-311+G****		**MP2/6-311+G****	
	C=O torsion	**C-O torsion**	**C=O torsion**	**C-O torsion**
V_0	0.520	0.000	0.271	0.000
V_1	-0.461	5.991	-0.189	5.819
V_2	11.025	8.589	10.817	8.741
V_3	-0.063	0.546	-0.098	0.637
V_4	-0.183	-0.174	-0.279	-0.463
V_5	0.002	0.048	0.009	0.027
V_6	0.007	0.009	-0.042	0.010

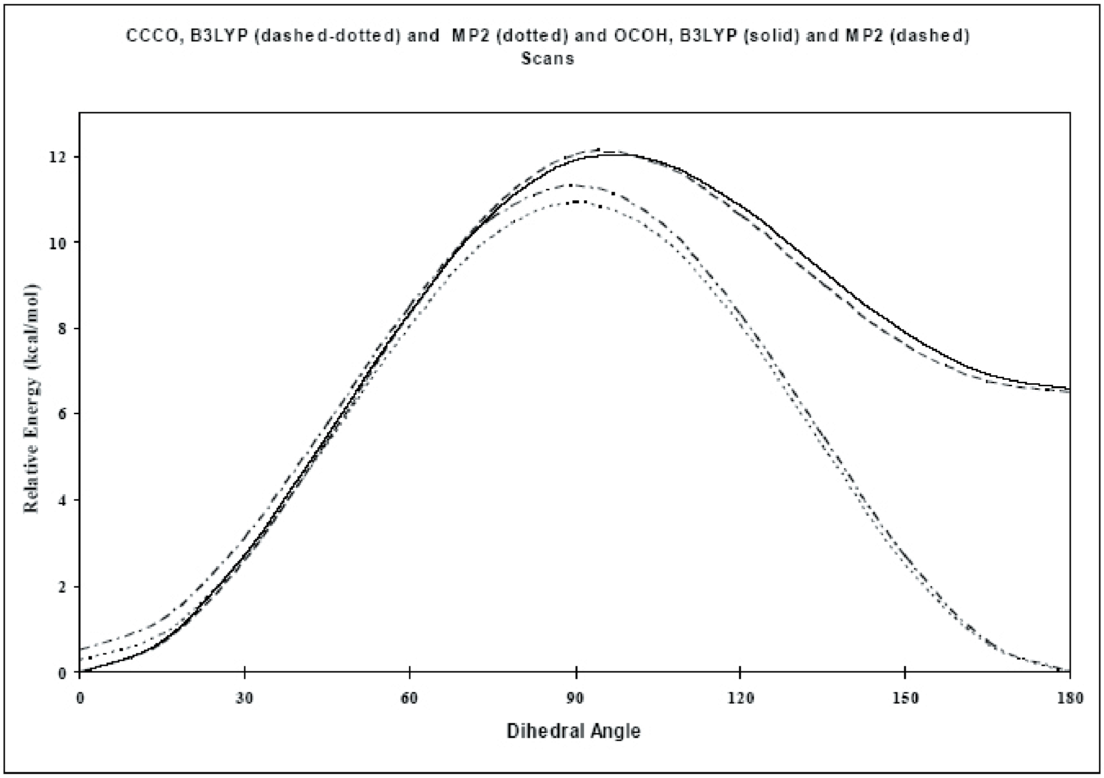

Figure 2. Potential curves for the C-C (dashed-dotted and dotted)) and C-O (solid and dashed) internal rotations in ketenecarboxylic acid as determined by DFT-B3LYP/6-311+G** and MP2/6-311+G** calculations, respetively.

Table 4. Symmetry coordinates of ketenecarboxylic acid.

Species	Description		Symmetry coordinate [a]
A'	CCO	antisymmetric stretch	$S_1 = P_1 - P_2$
	CCO	symmetric stretch	$S_2 = P_1 + P_2$
	C_2-H_7	stretch	$S_3 = T$
	C=O	stretch	$S_4 = D$
	O-H	stretch	$S_5 = Q$
	C-C	stretch	$S_6 = X$
	C-O	stretch	$S_7 = S$
	CCO	in-plane bend	$S_8 = \alpha$
	C_2-H_7	in-plane bend	$S_9 = \beta_2 - \beta_3$
	CO(OH)	deformation	$S_{10} = \delta_2 + \delta_3 - 2\delta_1$
	CO(OH)	rock	$S_{13} = \delta_2 - \delta_3$
	COH	in-plane bend	$S_{11} = \sigma$
	C=C-C	in-plane bend	$S_{12} = 2\beta_1 - \beta_2 - \beta_3$
A"	C-H	wag	$S_{14} = \omega$
	C-O	wag	$S_{15} = \omega$
	OCC	wag	$S_{16} = \xi$
	O-H	torsion	$S_{17} = \chi$
	C=O	torsion	$S_{18} = \tau$

[a] Not normalized.

Table 5. Calculated vibrational frequencies[a] of *trans* ketenecarboxylic acid at B3LYP/6-311+G** level.

Sym.	**No.**	**Freq.**	**IR int.**	**Raman act**	**Depol. ratio**	**PED**
A’	ν_1	3779	102.80	88.84	0.25	100% S_5 (O-H str.)
	ν_2	3224	23.86	71.92	0.25	100% S_3 (C_2-H_7 str.)
	ν_3	2234	849.47	16.63	0.73	96% S_1 (CCO antisym str.)
	ν_4	1795	710.46	44.84	0.27	83% S_4 (C=O str.)
	ν_5	1405	94.98	4.82	0.13	34% S_2 (CCO sym str.), 23% S_6 (C-C str.), 15% S_9 (C_2-H_7 in-plane bend)
	ν_6	1321	34.30	2.88	0.28	31% S_{11} (COH in-plane bend), 20% S_9 (C_2-H_7 in-plane bend), 17% S_{10} (CO(OH) def), 14% S_2 (CCO sym str.), 14% S_7 (C-O str.)
	ν_7	1178	291.77	9.02	0.42	45% S_{11} (COH in-plane bend), 21% S_7 (C-O str.), 15% S_6 (C-C str.)
	ν_8	1115	45.16	13.01	0.21	48% S_9 (C_2-H_7 in-plane bend), 32% S_2 (CCO sym str.)
	ν_9	902	20.28	8.39	0.11	51% S_7 (C-O str.), 28% S_6 (C-C str.)
	ν_{10}	676	27.00	7.32	0.12	27% S_8 (CCO in-plane bend), 19% S_{13} (CO(OH) rock), 18% S_{12} (C=C-C in-plane bend), 17% S_{10} (CO(OH) def)
	ν_{11}	529	20.58	2.70	0.26	50% S_{10} (CO(OH) def), 21% S_6 (C-C str.), 11% S_8 (CCO in-plane bend)
	ν_{12}	423	6.16	1.38	0.65	55% S_{13} (CO(OH) rock), 28% S_8 (CCO in-plane bend), 12% S_{10} (CO(OH) def)
	ν_{13}	147	2.02	1.51	0.65	64% S_{12} (C=C-C in-plane bend), 21% S_8 (CCO in-plane bend), 15% S_{13} (CO(OH) rock)
A”	ν_{14}	770	71.22	0.57	0.75	73% S_{14} (C-H wag), 20% S_{17} (O-H torsion)
	ν_{15}	583	0.00	2.25	0.75	80% S_{15} (C-O wag), 13% S_{16} (OCC wag)
	ν_{16}	552	42.70	0.03	0.75	80% S_{17} (O-H torsion), 20% S_{14} (C-H wag)
	ν_{17}	528	99.80	0.83	0.75	82% S_{16} (OCC wag), 15% S_{15} (C-O wag)
	ν_{18}	107	0.83	0.22	0.75	100% S_{18} (C=O torsion)

[a] IR intensities and Raman activities are calculated in km mol^{-1} and Å^4 amu^{-1}, respectively.

Discussion

Ketenes are found to be fundamental starting materials or stable intermediates in many important chemical reactions. They are capable to undergo (2+2) cycloaddition reaction with different unsaturated compounds and nucleophilic addition reactions with different nucleophiles (20-26). Tidwell *et al.* reported that the primary stabilizing influence of substituents on ketenes is by σ-electron donation to the electronegative ketene group (2). It was also reported that there is evidence that subsituents stabilize ketenes by π acceptance and not by n-π donation.

The interesting properties of ketenes and ketenecarboxylic acid in particular and its derivatives (2, 17, 18) turned the attention to investigate its structure by theoretical DFT and MP2 calculations in the present study. From the energy optimization, ketenecarboxylic acid was predicted to have planar structure for the low energy forms. The potential curve of the CCCO and OCOH internal rotations in ketenecarboxylic acid was consistent with the *trans* (the CCCO dihedral angle is 180º) and the *cis* (the CCCO dihedral angles is 0º) minima, where the OCOH dihedral angle is 0º (Figure 2). The two planar conformations were predicted to have C-C and C-O rotational barriers of about 10 and 12 kcal/mol (Figure 2). The stability of the planar forms of ketenecarboxylic acid is a result of pronounce conjugation between the ketene and the carbonyl groups as in formyl ketene (12).

The equilibrium constant *k* for the *cis* ↔ *trans* conformational interconversion in ketenecarboxylic acid was estimated from the change in the Gibb’s free-energy as follows:

Table 6. Calculated vibrational frequencies^a of *cis* ketenecarboxylic acid at B3LYP/6-311+G** level.

Sym.	**No.**	**Freq.**	**IR int.**	**Raman act**	**Depol. ratio**	**PED**
A’	ν_1	3772	103.00	98.28	0.24	100% S_5 (O-H str.)
	ν_2	3213	21.90	79.10	0.22	100% S_3 (C_2-H_7 str.)
	ν_3	2242	844.45	14.99	0.75	96% S_1 (CCO antisym str.)
	ν_4	1770	417.15	22.72	0.23	83% S_4 (C=O str.)
	ν_5	1446	267.21	10.43	0.21	26% S_6 (C-C str.), 26% S_2 (CCO sym str.), 23% S_9 (C_2-H_7 in-plane bend)
	ν_6	1308	0.43	6.12	0.08	53% S_{11} (COH in-plane bend), 34% S_2 (CCO sym str.)
	ν_7	1140	346.69	3.21	0.61	42% S_7 (C-O str.), 25% S_2 (CCO sym str.), 20% S_{11} (COH in-plane bend)
	ν_8	1110	111.45	9.73	0.31	56% S_9 (C_2-H_7 in-plane bend), 13% S_7 (C-O str.), 13% S_7 (C-O str.), 13% S_2 (CCO sym str.)
	ν_9	947	13.24	8.64	0.04	43% S_6 (C-C str.), 14% S_{12} (C=C-C in-plane bend), 10% S_8 (CCO in-plane bend)
	ν_{10}	689	23.40	10.13	0.23	37% S_{10} (CO(OH) deformation), 22% S_7 (C-O str.), 18% S_8 (CCO in-plane bend), 11% S_{12} (C=C-C in-plane bend)
	ν_{11}	516	14.83	1.40	0.11	35% S_{10} (CO(OH) deformation), 28% S_8 (CCO in-plane bend), 19% S_6 (C-C str.)
	ν_{12}	414	8.57	0.86	0.62	68% S_{13} (CO(OH) rock), 19% S_8 (CCO in-plane bend)
	ν_{13}	141	0.42	2.86	0.62	64% S_{10} (C=C-C in-plane bend), 19% S_8 (CCO in-plane bend)
A”	ν_{14}	770	64.69	0.18	0.75	84% S_{14} (C-H wag), 11% S_{17} (O-H torsion)
	ν_{15}	603	8.23	2.99	0.75	52% S_{16} (OCC wag), 48% S_{17} (O-H torsion)
	ν_{16}	575	21.87	0.43	0.75	89% S_{15} (C-O wag)
	ν_{17}	514	112.61	0.48	0.75	46% S_{17} (O-H torsion), 38% S_{16} (OCC wag)
	ν_{18}	113	0.00	0.38	0.75	93% S_{18} (C=O torsion)

^{a}IR intensities and Raman activities are calculated in km mol^{-1} and Å^4 amu^{-1}, respectively.

$$k = \frac{g_{cis}}{g_{trans}} e^{-\Delta G / RT} \;;\; \Delta G = G_{cis} - G_{trans} \qquad (1)$$

where, each of the two conformes is one-fold degenerate ($g_{cis}/g_{trans} = 1$) and R is 8.314 J mol^{-1} K^{-1}. From the calculations G_{cis} is -341.270973 H and G_{trans} is -341.271811 H, that gives rise to a calculated Gibb’s free energy difference, ΔG, of 0.5259 kcal/mol (2.2002 kJ/mol) and an equilibrium constant k of 0.4117 at 298.15 K that corresponds to an equilibrium mixture of about 29% cis and 71% trans of ketenecarboxylic acid at 298.15 K.

The vibrational wavenumbers of ketenecarboxylic acid in its stable *trans* and *cis* conformations are listed in Tables 5 and 6. The vibrational modes associated with the ketene -CH=C=O moiety were compared to the corresponding ones observed for *trans*-chlorocarbonyl ketene (19). The vibrational assignments of most of the fundamental vibrations were straightforward based on the calculated PED values, and several of the calculated modes especially bending ones were predicted to noticeably mix with other modes as given in Tables 5 and 6.

The two C-H and the O-H stretching modes (S_3 and S_5) were calculateted to have no degree of mixing in the spectra of *trans* and *cis* of ketenecarboxylic acid (Tables 5 and 6). The C-H stretching mode of the ketene group (S_3) was calculated at 3224 cm^{-1} (Table 5). The two C-H bending modes (S_9 and S_{14}) were calculated at 1115 cm^{-1} (48% PED) and 770 cm^{-1} (73% PED) as shown in Table 5. The corresponding A’ C-H in-plane bend was observed at 1051 cm^{-1} in the spectrum of chlorocarbonyl ketene (19).

The vibrational mode with the highest calculated infrared intensity in the molecule was calculated at 2234 cm^{-1} (96% PED) and assigned with confidence to the antisymmetric C=C=O stretch that agrees with the observed intense band at 2160 cm^{-1} for chlorocarbonyl ketene (19). The symmetric C=C=O stretch (S_2) could be assigned to the calculated wavenumber at 1405 cm^{-1} that agrees with the observed one at 1376 cm^{-1} in the spectrum of chlorocarbonyl ketene (19).

The C-C and C-O strectching modes and several of the bending modes were predicted to extensively mix with other vibrations as shown in Tables 5 and 6 and their assignment could not be made on the basis of only their calculated PED values. However, the lowest vibrational torsional mode in the spectra of the *trans* conformation of ketenecarboxylic acid was calculated at 107 cm^{-1} with 100% PED (Table 5). This mode was predicted at 113 cm^{-1} (93% PED) in the spectrum of the *cis* conformer of the molecule (Table 6).

Conclusion

In conclusion, ketenecarboxylic acid was predicted by both DFT-B3LYP/6-311+G** and MP2/6-311+G** calculations to exist predominantly in the *trans* conformation at ambient temperature. High C-C and C-O rotational barriers of about 10 and 12 kcal/mol were calculated at the two levels and attributed to pronounced conjugation effects in the molecule. Reliable vibrational assignments for the normal modes of ketenecarboxylic acid were provided on the basis of normal coordinate analyses.

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