

Density Functional Calculations, Structure, and Vibrational Frequencies of 2-Cyclopenten-1-one in Its S_0 , $S_1(n,\pi^*)$, $T_1(n,\pi^*)$, and $T_2(\pi,\pi^*)$ States[†]

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Density functional calculations have been carried out on the S_0 , $S_1(n,\pi^*)$, and $T_1(n,\pi^*)$ states of 2-cyclopenten-1-one (2CP) to complement the experimental study of the triplet state using cavity ringdown spectroscopy described in the previous paper. Structures and vibrational frequencies were calculated for each state at both the B3LYP/6-31+G(d,p) and B3LYP/6-311+G(d,p) levels. The structural information was used to obtain the kinetic energy part of the ring-bending Hamiltonian, for the analysis of triplet-state spectral data. The density functional calculations show the molecule in its S_0 and S_1 states to be planar, but to have a small barrier to planarity in the $T_1(n,\pi^*)$ triplet state. This is in line with potential-energy fits to the experimental ring-bending levels for each state. The calculated barrier for the $T_2(\pi,\pi^*)$ state is 999 cm^{-1} . This provides further confirmation that the cavity ringdown data, from which a 43-cm^{-1} barrier was determined, correspond to the $T_1(n,\pi^*)$ state. The calculated vibrational frequencies are in excellent agreement with the experimental data for the S_0 state and also for the most part for the S_1 and T_1 states. Notably, the frequency calculated for the very anharmonic ring-bending vibration cannot be expected to be very accurate.

Introduction

In the preceding paper,¹ the cavity ringdown (CRD) spectra of 2-cyclopenten-1-one (2CP) and two deuterated isotopomers were reported and analyzed. A number of vibrations in the $T_1(n,\pi^*)$ state were assigned, and the potential-energy function for the ring-bending vibration was fit to observed transition frequencies. The fitting procedure in that study required the molecular structure of the T_1 state in order to calculate the kinetic-energy (reciprocal reduced mass) expansion for the ring-bending Hamiltonian. The molecular structure was obtained from density functional (DFT) calculations that we describe in this paper. We also present the calculated vibrational frequencies for not only the $T_1(n,\pi^*)$ state but also for the S_0 and $S_1(n,\pi^*)$ states for which experimental data are also available.^{2–4} In addition, the results of calculations for the electronic excitation energies as well as for the barrier to planarity of the $T_1(n,\pi^*)$ and $T_2(\pi,\pi^*)$ states will be presented.

The infrared and Raman spectra of 2CP were previously reported by Chao and Laane,² and these are characteristic of a planar, conjugated molecule. The ring-bending (ring-puckering) vibration was found to be governed by a relatively stiff potential function with a single minimum, confirming that the molecule is planar in its S_0 electronic ground state.^{2,3} This gives rise to seven observed far-infrared bands in the $90\text{--}120\text{ cm}^{-1}$ region. Band satellites along with hot bands in the ring-twisting region ($285\text{--}295\text{ cm}^{-1}$) also allowed a two-dimensional potential-energy surface in terms of the puckering and twisting to be determined.³ The $S_1(n,\pi^*)$ state was investigated by Cheatham and Laane⁴ using jet-cooled fluorescence excitation spectroscopy. In addition to assigning 13 of the fundamental vibrational

frequencies, they also determined the one-dimensional ring-puckering potential-energy function for the d_0 , $5\text{-}d_1$, and $5,5\text{-}d_2$ isotopomers. This potential function showed that the molecule remains planar in its $S_1(n,\pi^*)$ state but has become considerably less rigid. The lowest puckering level lies 67 cm^{-1} above the vibrational ground state.

The 2CP molecule has been the subject of previous theoretical studies. The CASSCF procedure was used to calculate the energy minima for the lowest $^3(n,\pi^*)$ and $^3(\pi,\pi^*)$ states,⁵ whereas both CIS and DFT techniques investigated the vertical and adiabatic excitation energies.⁶ The integrated molecular orbital and molecular mechanics (IMOMM) approach was also used⁷ to study the adiabatic triplet excitation energies of 2CP and other molecules. None of these studies included a calculation of vibrational frequencies. However, given the previous lack of experimental data for the $T_1(n,\pi^*)$ state, it would not have been possible to evaluate the accuracy of either calculated frequencies or excitation energies. The CRD data reported in the foregoing paper¹ now provide experimental frequencies for several low-frequency modes of the T_1 state. This provides a test of some of the calculated frequencies reported in the present study, as well as the calculated ring-bending potential-energy function. The CRD data also permit an experimentally based estimate of adiabatic excitation energy, which may be used to test corresponding predictions of the present as well as previous^{4–6} computational studies.

Computational Methods

All calculations were performed using the Gaussian 98 program.⁸ The geometries of 2CP in its S_0 , S_1 , T_1 , and T_2 electronic states were fully optimized using the B3LYP method with the 6-31+G(d,p) and 6-311+G(d,p) basis sets. Both singlet and triplet states of 2CP were generated by selecting the appropriate orbital occupancies as an initial guess. By examining the vibrational frequencies, all equilibrium geometries of the

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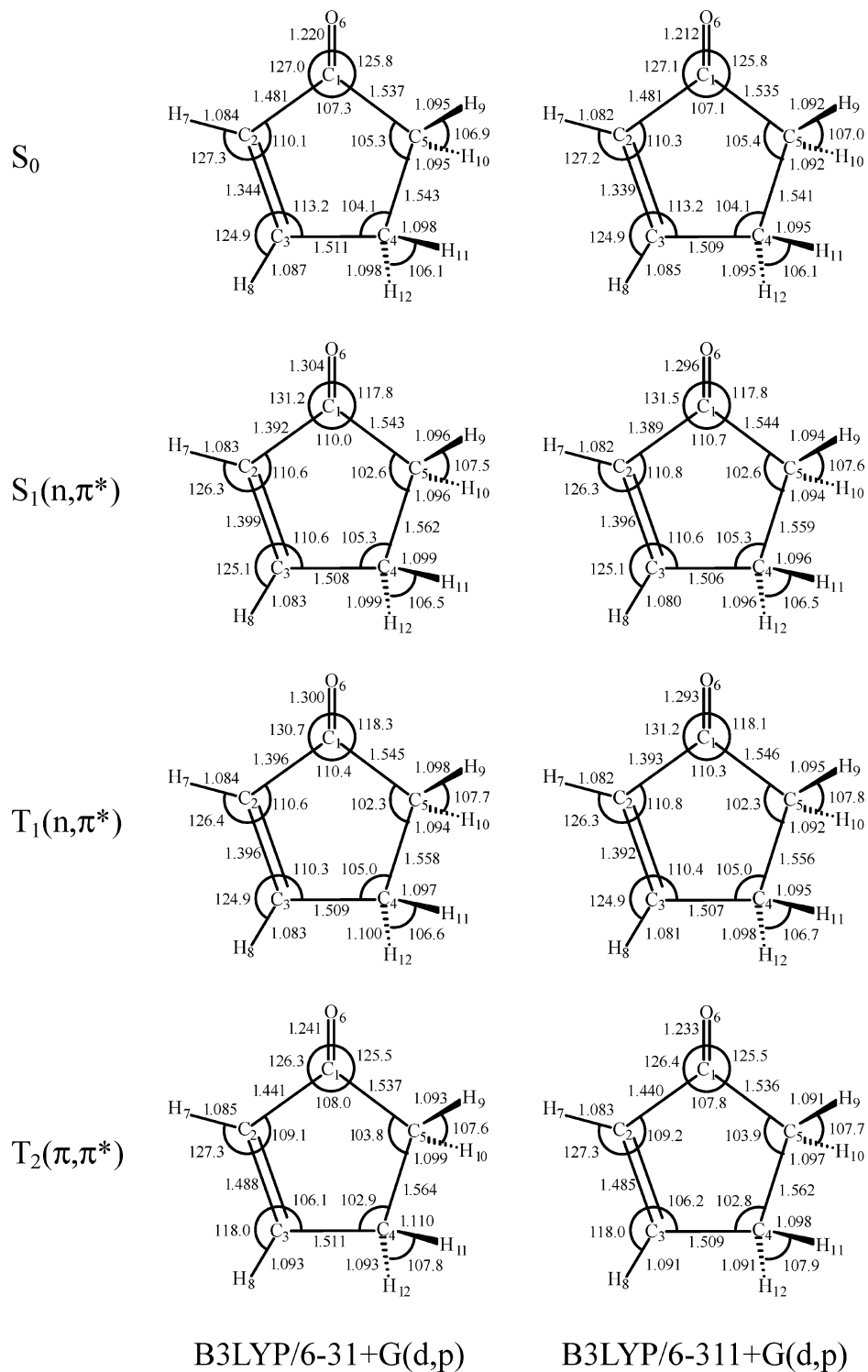


Figure 1. Calculated geometries of 2-cyclopenten-1-one in its ground and excited states.

ground and excited states were confirmed to be local minima. The calculated vibrational frequencies of each state were scaled⁹ by 0.985, except for the C–H stretching modes where 0.964 was utilized.

Previous computational studies of enone excited states have used both CIS and DFT methods. In a study of enone photochemistry, Uppili et al.¹⁰ utilized the CIS(D) method, which includes a size-consistent doubles correction to the previously reported CIS method.^{11,12} Sunoj et al.⁶ performed CIS and DFT calculations to illustrate the influence of lithium cation complexation on vertical excitation energies of enones. In the present work, we also performed DFT (B3LYP) studies,

in separate calculations with different basis sets, to investigate the conformational dynamics and spectral properties of 2CP in its S_0 , S_1 , and T_1 electronic states. The ring-bending barriers and vibrational frequencies of 2CP in each electronic state were determined for comparison to spectroscopic data.

Results and Discussion

Figure 1 shows the calculated geometrical parameters for the S_0 , $S_1(n,\pi^*)$, $T_1(n,\pi^*)$, and $T_2(\pi,\pi^*)$ states based on both the B3LYP/6-31+G(d,p) and B3LYP/6-311+G(d,p) basis sets. The calculated (B3LYP/6-311+G(d,p)) ground-state structure gives

TABLE 1: Calculated and Experimental Rotational Constants (GHz) of 2-Cyclopenten-1-one

		A	B	C
B3LYP/6-311+G(d,p)	S ₀	7.434	3.581	2.491
	S ₁ (n,π*)	7.440	3.516	2.460
	T ₁ (n,π*) (puckered)	7.442	3.524	2.469
	T ₁ (n,π*) (planar)	7.434	3.520	2.462
	T ₂ (π,π*) (puckered)	7.422	3.481	2.516
	T ₂ (π,π*) (planar)	7.524	3.421	2.421
experimental ^a	S ₀	7.410	3.586	2.493

^a Reference 13.**TABLE 2: Calculated Excitation Energy and Ring-Puckering Barrier of 2-Cyclopenten-1-one**

	excitation energy (cm ⁻¹)			barrier (cm ⁻¹)	
	S ₁ (n,π*)	T ₁ (n,π*)	T ₂ (π,π*)	T ₁ (n,π*)	T ₂ (π,π*)
B3LYP/6-31+G(d,p)	24 937	24 362	24 462	14	977
B3LYP/6-311+G(d,p)	25 073	24 497	24 740	8	999
experimental	28 130 ^a	26 830 ^a		43	

^a Derived from observed electronic band origin and observed (ground-state) and calculated (excited-state) zero-point energies.

rise to rotational constants of $\bar{A} = 0.2480$ cm⁻¹, $\bar{B} = 0.1194$ cm⁻¹, and $\bar{C} = 0.0831$ cm⁻¹, which may be compared to the experimental microwave values of 0.2472, 0.1196, and 0.0832 cm⁻¹, respectively.¹³ This excellent agreement helps one to confirm that the calculated S₀ structure is very accurate. Table 1 presents the calculated rotational constants (GHz) for each of the three electronic states. A previous MOPAC-AM1 computation¹³ reported bond lengths which generally differ by less than ±0.02 Å from those of our B3LYP/6-311+G(d,p) calculation. However, the C₂-C₃-C₄ and C₃-C₄-C₅ angles differ by more than 4° each.

As can be seen in Figure 1, the C=O bond length increases from 1.212 Å in the ground state (B3LYP/6-311+G(d,p) calculation) to 1.296 Å in S₁(n,π*) and 1.293 Å in T₁(n,π*). Sunoj et al.⁶ (B3LYP/6-31+G(d) calculation) report 1.21 Å for the ground state and 1.30 Å for the triplet. The C=C bond length increases from 1.339 Å (S₀) to 1.396 Å (S₁) and 1.392 Å (T₁) resulting from the excitation to the antibonding orbital. Sunoj et al. give 1.34 Å (S₀) and 1.39 Å (T₁). The C₁-C₂ bond between the C=O and C=C bonds decreases from 1.481 Å (S₀) to 1.389 Å (S₁) and 1.393 Å (T₁), reflecting that this bond has strengthened to be on par with C₂=C₃. Very little difference can be seen in the geometrical parameters between S₁ and T₁ except that the molecule is calculated to be slightly puckered in the triplet state, in line with the experimental observations.¹ The calculation indicates a dihedral angle of puckering of 10.2° as compared to the experimental value of 12°.

Figure 1 also shows that the geometry of the T₂(π,π*) state is very different from the other two excited states shown, as well as the ground state. The C=O bond distance of 1.233 Å is much closer to that of the ground state (1.212 Å) rather than those of S₁(n,π*) and T₁(n,π*), where the bond has become elongated. This indicates that the antibonding character for the T₂(π,π*) state is primarily in the C=C bond rather than the C=O bond. Its C=C distance of 1.485 Å is also much larger than those for the other three states shown, thus supporting this interpretation. The increased C=C distance is also consistent with the reduction in bond order to be expected when a π (bonding), rather than a nonbonding electron, is promoted to a π* orbital.

Similar changes in bonding are predicted¹⁴ to occur in the prototypical enone acrolein (CH₂=CH-CH=O). Ab initio calculations^{14a} show that the lowest ³(π,π*) state of acrolein

TABLE 3: Observed and Calculated Frequencies (cm⁻¹) for 2-Cyclopenten-1-one in the S₁(n,π*), T₁(n,π*), and T₂(π,π*) States

mode	S ₀		S ₁ (n,π*)		T ₁ (n,π*)	T ₂ (π,π*)	
	exp. ^a	6-311 ^b	exp. ^c	6-311 ^b	6-311 ^b	6-311 ^b	
a'	1	3083	3090		3098	3096	3079
	2	3067	3051		3080	3079	2980
	3	2938	2940		2915	2899	2905
	4	2885	2907		2884	2874	2877
	5	1748	1750	1418	1472	1469	1540
	6	1599	1616	1357	1451	1450	1461
	7	1452	1461		1419	1415	1441
	8	1418	1430		1368	1370	1292
	9	1345	1346		1319	1322	1279
	10	1305	1303		1258	1260	1259
	11	1232	1239		1222	1234	1242
	12	1173	1164		1058	1058	1153
	13	1094	1093	1037	1034	1036	1039
	14	999	989	974	969	967	919
	15	912	905	906	892	895	903
	16	822	812		810	821	789
	17	753	751	746	748	734	665
	18	630	623	587	581	579	576
	19	464	459	348	342	340	445
a''	20	2980	2977		2948	2958	2975
	21	2927	2928		2900	2915	2960
	22	1208	1214		1189	1179	1183
	23	1138	1142		1111	1110	1111
	24	1007	1012		977	977	965
	25	960	975	849 ^d	854	848	859
	26	(815) ^e	815	768	785	785	726
	27	750 ^f	757		491	504	533
	28	532	534	422	416	407	454
	29	287	291	274	253	226	219
	30	94	102	67	25	86	156

^a Reference 2. ^b B3LYP/6-311 + G** basis set. ^c Reference 4. ^d 849 cm⁻¹ was previously assigned to ν₁₆. ^e Estimated. ^f The 750-cm⁻¹ band was previously assigned to ν₂₆.

has a diradical electronic structure, $\dot{\text{C}}\text{H}_2-\dot{\text{C}}\text{H}-\text{CH}=\text{O}$. The terminal CH₂ group twists 90° out of the molecular plane, thereby minimizing repulsion between lone electrons in adjacent p-like orbitals. This type of conformational change preferentially stabilizes the ³(π,π*) state so that it is lower in energy than the ³(n,π*) state in acrolein and analogous flexible enones.¹⁵ In 2CP, the conformational mobility is not so extreme, due to the geometrical constraints of the ring, and the two triplet states are seen in the present work (Table 2) to be nearly isoenergetic.

Nonetheless, the T₂(π,π*) state of 2CP shows a dramatic effect of having antibonding character localized within the ring. As seen in Table 2, the calculated barrier to planarity for the T₂(π,π*) state is 999 cm⁻¹. By contrast, the T₁(n,π*) state is predicted to have a tiny barrier to planarity (14 or 8 cm⁻¹, depending on basis set), in line with the experimental value¹ of 43 cm⁻¹. In the T₁(n,π*) state, the conjugation has been reduced from that of the ground or S₁(n,π*) state, whereas in the T₂(π,π*) state, the conjugation has been almost totally removed, and 2CP now resembles cyclopentanone, a ketone with a saturated five-membered ring. The barrier to planarity¹⁶ of cyclopentanone is 1408 cm⁻¹.

Because a full vibrational assignment for 2CP has been made for the ground state² and because a number of assignments are now available for the S₁(n,π*) and T₁(n,π*) states,^{1,4} it is of interest to compare the calculated frequencies from our DFT study to the experimental values. Table 3 presents the calculated vibrational frequencies for all four states along with the experimental data for the S₀ and S₁(n,π*) states. Table 4 presents vibrational descriptions for the low-frequency modes, along with calculated and (where available) experimental frequencies for the four states. As can be seen in Table 3, the agreement between the observed and calculated values is remarkably good. In fact,

TABLE 4: Low-Frequency Fundamentals (cm^{-1}) of 2-Cyclopenten-1-one

approximate description	S_0		$S_1(n,\pi^*)$		$T_1(n,\pi^*)$		$T_2(\pi,\pi^*)$
	exp. ^a	calc. ^b	exp. ^c	calc. ^b	exp. ^d	calc. ^b	calc. ^b
a' ν_{18} ring-bending	630	623	587	581		579	576
ν_{19} C=O wag (in-plane)	464	458	348	342	346	338	445
a'' ν_{27} β -CH ₂ rocking	750	757		491		504	533
ν_{28} C=O wag (out-of plane)	532	534	422	416	432	407	454
ν_{29} C=C twisting	287	291	274	253	239	226	219
ν_{30} ring-puckering	94	102	67	25	37	86	156

^a References 2 and 3. ^b B3LYP/6-311+G(d,p) basis set with scaling factor 0.985. ^c Reference 4. ^d Reference 1.

it is so consistently good that we felt it reasonable to reassign several frequencies, and these are indicated in Table 3. With a scaling factor of 0.985 for all of the vibrations other than the C–H stretches, the calculated frequencies agree on average with the experimental values to better than $\pm 7 \text{ cm}^{-1}$.

For the $S_1(n,\pi^*)$ state, the anharmonic ring-bending vibration (ν_{30}) at 67 cm^{-1} is fit poorly, as are the coupled C=O and C=C stretches at 1418 and 1357 cm^{-1} . The other eleven observed frequencies agree with the calculated values on average better than $\pm 8 \text{ cm}^{-1}$. For the $T_1(n,\pi^*)$ state the DFT calculation cannot be expected to provide the correct transition frequency for the double-minimum potential function, so the disagreement for ν_{30} is not unanticipated. The other three observed T_1 frequencies, however, are fit reasonably well ($\pm 15 \text{ cm}^{-1}$, compared to $\pm 11 \text{ cm}^{-1}$ for the same three frequencies in S_1).

Table 2 includes adiabatic excitation energies (T_e values) predicted for the excited states, as well as the corresponding values derived from observed spectroscopic band origins. The latter were obtained by removing the contributions due to ground- and excited-state zero-point energies from the observed origin band frequencies (T_0 values). For the ground state, the zero-point energy was determined directly from the experimental^{2,3} fundamental frequencies, regarding all 30 vibrations as harmonic. For the $S_1(n,\pi^*)$ and $T_1(n,\pi^*)$ states, the zero-point energies for ν_1 through ν_{29} were estimated by using experimental^{1,4} harmonic frequencies where available, supplemented by values calculated in the present DFT study. For the ring-bending mode (ν_{30}), the zero-point energy was determined from the potential fits reported previously.^{1,4} In the $S_1(n,\pi^*)$ and $T_1(n,\pi^*)$ zero-point energy determinations, the uncertainty in each calculated fundamental frequency was conservatively taken to be $\pm 15 \text{ cm}^{-1}$ (see the discussion above). This yielded experimentally based adiabatic excitation energies of $26\,830 \pm 80 \text{ cm}^{-1}$ for $T_1(n,\pi^*)$ and $28\,130 \pm 60 \text{ cm}^{-1}$ for $S_1(n,\pi^*)$.

Table 2 shows that the present DFT calculation underestimates the adiabatic excitation energy for both the $S_1(n,\pi^*)$ and $T_1(n,\pi^*)$ states. The deviations from experimental values are 3060 cm^{-1} (8.8 kcal/mol, or 0.38 eV) and 2330 cm^{-1} (6.7 kcal/mol, or 0.29 eV), respectively. The magnitude of these deviations is not unexpected for DFT calculations. A recent report¹⁷ evaluates the accuracy of adiabatic excitation energies calculated by time-dependent density functional theory (TDDFT) for a variety of excited states and molecules. For a molecule as small as formaldehyde, the computed adiabatic excitation energy deviates from the experimental value by -0.39 eV for T_1 and $+0.11 \text{ eV}$ for S_1 . Yet the excited-state structural parameters and vibrational frequencies calculated for formaldehyde are very accurate (typically $\pm 0.02 \text{ \AA}$ deviation in bond lengths and $< 50 \text{ cm}^{-1}$ in vibrational frequencies), a characteristic that is shared in the present DFT study of 2CP.

Table 5 compares the experimental excitation energy of the 2CP $T_1(n,\pi^*)$ state with predictions from all of the reported calculations. The Hartree–Fock-based (ab initio) methods

TABLE 5: Calculated and Experimental Adiabatic Excitation Energy of the $T_1(n,\pi^*)$ State of 2-Cyclopenten-1-one

method	excitation energy	
	eV	1000 cm^{-1}
CASSCF ^a	3.25	26.2
IMOMO ^b	3.40	27.2
B3YLP/6-31+G(d) ^c	3.02	24.4
B3YLP/6-31+G(d,p) ^d	3.02	24.4
B3YLP/6-311+G(d,p) ^d	3.04	24.5
experiment ^e	3.326	26.83

^a Reference 5. ^b Reference 7. ^c Reference 6. ^d This work. ^e Reference 1.

provide more accurate excitation energies than DFT approaches. It should be noted, of course, that correlated ab initio calculations are computationally more expensive than DFT and are prohibitively so for large (> 20 atom) molecules.

Conclusions

The density functional calculations reported in this paper very nicely complement the experimental results in the previous paper,¹ as well as in the earlier ground state^{2,3} and $S_1(n,\pi^*)$ ⁴ excited-state investigations. The $T_1(n,\pi^*)$ state is calculated to be slightly lower in energy than the $T_2(\pi,\pi^*)$ state and has only a tiny barrier to planarity as compared to a high one (999 cm^{-1}) in the $T_2(\pi,\pi^*)$ state. Thus, the CRD data, which establish a 43-cm^{-1} barrier, clearly arise from transitions to $T_1(n,\pi^*)$. The calculated vibrational frequencies for the S_0 state compare extremely well with the observed values,^{2,3} whereas those for the $S_1(n,\pi^*)$ and $T_1(n,\pi^*)$ states are quite satisfactory. This outcome appears to be typical for DFT calculations of excited states. Our results advocate the further use of DFT as a technique that is comparable in cost to CIS but superior in its ability to characterize the shapes of excited-state potential-energy surfaces.

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