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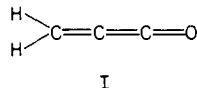
The Structure of Propadienone

Ronald D. Brown,* Robert Champion, Patricia S. Elmes, and Peter D. Godfrey

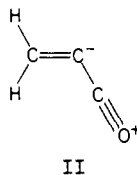
Contribution from the Department of Chemistry, Monash University, Clayton, Victoria, Australia 3168. Received January 4, 1985

Abstract: A reanalysis of the vibrational ground-state microwave spectra of various isotopic versions of propadienone including lines assigned to the new $1\text{-}^{13}\text{C}$ isotope, and taking into account the molecular nonrigidity, has been undertaken in order to determine more precisely the molecular structure. The nonlinear heavy-atom chain is found to have a zigzag conformation with angles $\angle\text{C}_1\text{C}_2\text{C}_3 = 144.5^\circ$ and $\angle\text{OC}_1\text{C}_2 = 169.4^\circ$. The vibrational potential function corresponding to this unusual structure has aspects that can be linked with structural features of a number of related molecules.

We previously reported^{1,2} conclusive evidence based on the analysis of vibrational ground-state microwave spectra that the equilibrium structure of propadienone (I) does not have the expected C_{2v} symmetry but has a nonlinear heavy-atom chain. An



r_0 structure was derived from experimentally determined B and C rotational constants for the isotopic variants: H_2CCCO , $\text{H}_2^{13}\text{CCCO}$, $\text{H}_2\text{CCC}^{18}\text{O}$, and the distinct monodeuterio conformers (*E*)- HDCCCO and (*Z*)- HDCCCO (previously designated *trans* and *cis* respectively). This data set was insufficient to establish independently the two heavy-atom chain bond angles, so following the suggestion provided by resonance structure arguments that canonical form II would be the most important one having a nonlinear heavy-atom chain, $\angle\text{OC}_1\text{C}_2$ was constrained to 180° .



The best-fit structure, obtained by least-squares fitting the remaining structural parameters to the observed rotational constants, was found to be bent some 30° away from linearity at the C_2 atom.

We report here a more completely determined set of structural parameters resulting from a more sophisticated treatment of the data which has been augmented with the recently observed microwave spectrum of the $\text{H}_2\text{C}^{13}\text{CO}$ isotopic species. The treatment differs from that previously employed in that it uses an elaborate rotation-vibration model to remove vibrational con-

tributions from the derived effective rotational constants.

Nonrigidity of Propadienone. The assignment of microwave region vibrational satellite spectra and also a number of intersystem transitions revealed that a barrier 364 cm^{-1} high separates the equivalent bent conformations of propadienone. A detailed account of the analysis of the rotation-vibration spectrum will appear in a forthcoming publication.³ The barrier although rising well above the ground vibrational state is not impenetrable and thus propadienone falls in the class of flexible or nonrigid molecules. Tunnelling through the barrier (i.e., interconversion) produces a small splitting (3.7 GHz) of the ground state into a pair of vibrational states (labeled $\nu_{12} = 0,1$) somewhat analogously to the case of ammonia. The rate of interconversion is, however, 40 times slower than a typical rotation and thus nonrigidity only slightly influences the ground-state rotational and structural parameters.

There are two considerations of importance in the context of determining the molecular structure, given the presence of tunnelling. Firstly, we needed to reassess a number of previously reported microwave line measurements, taking into account the barely resolvable doubling of the rotational transitions arising from the split vibrational ground state. Only transitions involving $K_a \geq 2$ needed reconsideration, and the small changes had an insignificant effect on the derived rotational constants. Secondly, the contribution of internal angular momentum associated with the tunnelling motion had to be removed from the effective ground-state rotational constants so that these could be treated in structural determinations on an equal footing with those from noninverting semirigid molecules.

Experimental Section

$[1\text{-}^{13}\text{C}]$ Propadienone was generated by flash vacuum pyrolysis of acrylic $[1\text{-}^{13}\text{C}]$ anhydride.

Acrylic $[1\text{-}^{13}\text{C}]$ Anhydride. $[^{13}\text{C}]$ Carbon dioxide, prepared from barium carbonate (90% ^{13}C , 4.04 g, 0.02 mol) and concentrated sulfuric acid (30 mL) and condensed in a liquid nitrogen trap on a vacuum line, was admitted to a cooled (-10°C), well-stirred tetrahydrofuran (THF) solution of vinylmagnesium bromide (70 mL, 0.292 M). The reaction

(1) Brown, R. D.; Godfrey, P. D.; Champion, R.; McNaughton, D. *J. Am. Chem. Soc.* **1981**, *103*, 5711-5715; **1982**, *104*, 6167.

(2) Brown, R. D. *J. Mol. Struct.* **1983**, *97*, 293-302.

(3) Brown, R. D.; Champion, R.; Godfrey P. D., to be published.

Table I. Rotational and Centrifugal Distortion Constants for the Isotopic Variants of Propadienone Determined from Their Spectra^a

	H ₂ CCCO	H ₂ CCC ¹⁸ O	H ₂ CC ¹³ CO	H ₂ ¹³ CCCO	(<i>E</i>)-HDCCCO	(<i>Z</i>)-HDCCCO
<i>A</i> ^b	143807 (1406)	160249 (2382)	155643 (2213)	144753 (3223)	139122 (1859)	107397 (1317)
<i>B</i> + <i>C</i>	8645.1659 (16)	8218.7526 (29)	8618.7698 (15)	8389.2989 (49)	8125.8322 (29)	8287.1606 (59)
<i>B</i> - <i>C</i>	128.9287 (38)	116.8966 (60)	128.1466 (32)	122.3147 (159)	123.6837 (81)	168.7443 (153)
<i>D</i> _{<i>J</i>}	0.001507 (26)	0.001456 (39)	0.001718 (40)	0.001098 (130)	0.001057 (59)	0.001795 (132)
<i>D</i> _{<i>JK</i>}	-0.78406 (27)	-0.74422 (50)	-0.79102 (91)	-0.77827 (132)	-0.42720 (79)	-0.46233 (154)
<i>d</i> _{<i>i</i>}	-0.000204 (27)	-0.000192 (36)	-0.000137 (36)	-0.000207 (152)	0.000013 (78)	-0.000141 (154)
<i>H</i> _{<i>KJ</i>}	-0.003038 (14)	-0.002954 (32)	-0.003593 (86)	-0.002988 (123)	-0.000424 (78)	-0.001278 (142)

^aUncertainties shown in parentheses are 1 standard deviation from the least-squares fit. All values quoted are in MHz with the uncertainties, as elsewhere in this work, in units of the least significant digit of the quoted number. ^bUncertainties in *A* are unreliable. The more detailed rotation-vibration analysis³ indicates that *A* = 153 524 (200) MHz for the main species, suggesting errors of the order of 10 GHz in the estimates of *A* in this table.

mixture was stirred for a further 30 min after the carbon dioxide trap had warmed to room temperature and then treated with cooled, dilute hydrochloric acid (10 mL). The THF layer was separated and stabilized with hydroquinone; the aqueous layer was extracted with ether (2 × 10 mL). The combined THF and ether extracts were washed with water and dried (MgSO₄) and the solvents evaporated under vacuum. [1-¹³C]Acrylic acid obtained as a colorless liquid by trap-to-trap distillation was shown by GLC analysis (6 ft × 1/8 in., 15% carbowax 20M on acid washed D.M.C.S. Chromosorb W (80–100), column programmed 100–200 °C at 10 °C/min) to contain 10% THF. The acid from three preparations (1.08 g, 15 mmol), stabilized with hydroquinone and without further purification, was dissolved in ether (15 mL), cooled (-10 °C), and treated with triethylamine (1.5 g, 15 mmol) followed by an ethereal solution (15 mL) of acryloyl chloride (1.35 g, 15 mmol) at such a rate that the temperature of the reaction mixture was maintained below 0 °C. The mixture was stirred for a further 5 min at 0 °C before the triethylammonium chloride was removed by filtration under nitrogen. The ether was removed by rotary evaporation and the residue vacuum distilled to isolate the required anhydride which was identified by GLC and mass spectrometry. MS, *m/z* 127 (*m*⁺, absent), 99 (5), 98 (7), 73 (8), 72 (7), 56 (68), 55 (100).

Results

Rotational and centrifugal distortion constants were least-squares fitted to the microwave spectra with the *S*-reduced form of the rotational Hamiltonian as discussed previously.¹ The observed low *J* (0–5) ^a*R*-branch transition frequencies are available as Supplementary Material. Table I lists the derived rotational constants and centrifugal distortion constants. Correlation tables for the least-squares fits are available as supplementary material.

Internal Angular Momentum. The interpretation of rotational constants as inverse moments of inertia having structural significance incorporates the assumption that rotation-vibration interaction contributions to these constants are small and that the contributions are virtually independent of isotopic version. The rotation-vibration interaction contributions arising from the small-amplitude ν_{1-11} vibrational modes meet these conditions. However, the influence of internal angular momentum associated with the large-amplitude ν_{12} mode needs special consideration since it depends on the symmetry of the substituted molecule and on the rate of interconversion which is strongly isotope dependent. In order to examine the contribution of the internal angular momentum to the derived constants a choice of single-vibrational-state, dual-vibrational-state, or multi-vibrational-state approximations to the exact infinite rotation-vibration Hamiltonian matrix may be employed. The internal angular momentum operators mix the rotational wave functions in different vibrational states so that in the usual matrix formalism they are vibrationally off-diagonal. When rotational and vibrational (inversion tunnelling) energies are similar in magnitude, resonances occur and at least a dual-vibrational-state treatment is necessary, with the appropriate internal angular momentum operator directly linking the two states included.

Empirically it is clear that no such resonances occur in the ground state for propadienone since a single-vibrational-state treatment adequately fits the observed microwave spectrum. The derived parameters, however, necessarily contain small internal angular momentum contributions which may lead to erroneous structural parameters.

In the case of propadienone, where the large-amplitude motion occurs in the molecular plane, the internal angular momentum

Table II. The Rotational Constants Used To Calculate the Molecular Structure^a

	<i>B</i> (obsd)	<i>C</i> (obsd)	ΔC	<i>C</i> (corrected)
H ₂ CCCO	4387.047	4258.119	-0.387	4257.732
H ₂ CCC ¹⁸ O	4167.825	4050.928	-0.346	4050.582
H ₂ CC ¹³ CO	4373.458	4245.312	-0.380	4244.932
H ₂ ¹³ CCCO	4255.807	4133.492	-0.343	4133.149
(<i>E</i>)-HDCCCO	4124.758	4001.074	-0.002	4001.072
(<i>Z</i>)-HDCCCO	4227.953	4059.208	-0.002	4059.206

^aThe correction ΔC removes from *C* the contribution of internal angular momentum associated with nonrigidity.

is directed along the *c* principal axis, and to a good approximation only the value of the *C* rotational constant is affected.

In principle, perturbation methods⁴ provide a means of estimating the contribution to *C*, but this approach would require the measurement and analysis of vibrational satellites for each of the isotopic species. For a transient species like propadienone the attendant requirement for large quantities of expensive labeled precursors makes this approach impracticable. In this work the more convenient alternative of a multi-vibrational-state treatment (a generalization of the semirigid bender model⁵), described in detail elsewhere,³ which accurately reproduces both the main species vibrational satellite spectra and also the ground-state spectra for each of the isotopically substituted versions, was employed. This method solves the Schrödinger equation explicitly for the rotation-vibration motion associated with the ν_{12} mode and assumes that the molecular parameters are simply averaged over the other vibrational modes.

The best-fit molecular structural parameters and ν_{12} potential function obtained by fitting the observed microwave spectra alone were then used with the same treatment to generate the theoretical spectra for the ground and excited ν_{12} states of the isotopically labeled species. These theoretical spectra were then treated as pseudoobservations for which the ground-state $\nu_{12} = 0$ spectrum and the $\nu_{12} = 0, 1$ spectrum pair were fitted with the single- and dual-vibrational-state models, respectively. In the latter case the internal angular momentum operator that links the two states, the magnitude of which was derived from the theoretical model, was included. The difference between the best-fit values of *C* obtained by the two methods for each isotope is the estimate of the contribution to *C* of internal angular momentum associated with interconversion for that isotopic form. The same procedure applied to the observed spectra for $\nu_{12} = 0, 1$ of the main species, and using an experimentally determined estimate of the internal angular momentum parameter, that was available from the analysis of higher vibrational states, showed that the correction to *C* determined from the theoretical model is overestimated by 5%. The same error was assumed for each isotopic version, and the theoretical corrections were scaled appropriately. The values of the rotational constants *B* and *C* and the corrections are presented in Table II.

The corrections show an expected slight isotopic dependence, but are negligible for the monodeuterio species. This is to be expected, because the mass asymmetry in this case quenches

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Table III. Coordinates of Nuclei (pm) Derived from Substitution Equations (r_s)^a and Those Calculated from r_0 Structures with ρ the Complement of $\angle C_1C_2C_3$ Fixed at the Value Shown

r_a	O	C ₁	C ₂	C ₃	H _E	H _Z
r_s	177.06	60.28	-66.09 ^b	-189.88	-208.10	-271.96
r_0 ($\rho = 34^\circ$)	177.14	61.11	-66.88	-190.02	-208.20	-272.00
r_0 ($\rho = 35.5^\circ$)	177.16	61.08	-66.87	-190.01	-208.28	-271.96
r_0 ($\rho = 37^\circ$)	177.19	61.02	-66.86	-189.99	-208.41	-271.92
r_b	O	C ₁	C ₂	C ₃	H _E	H _Z
r_s	-7.74	± 0.50	31.87, ^b 32.86	-16.29	-124.34	55.81
r_0 ($\rho = 34^\circ$)	-8.63	2.23	31.36	-16.36	-124.23	56.09
r_0 ($\rho = 35.5^\circ$)	-7.52	-0.27	32.03	-16.07	-123.93	56.40
r_0 ($\rho = 37^\circ$)	-6.15	-3.19	32.58	-15.61	-123.44	56.90

^a For the main species $I_a = 32919^3$ and $I_b = 1151979$ u pm². ^b r_s coordinates derived from moment equations (two values arise due to the indeterminacy of the sign of r_b for the C₁ nucleus).

Table IV. The rotational Constants (MHz) Calculated from the Principal Moments of Inertia of the Structure Shown in Figure 1 and Their Deviation from Those Listed in Table II

	B (calcd)	$o-c$	C (calcd)	$o-c$
H ₂ CCCO	4387.172	-0.125	4257.820	-0.083
H ₂ CCC ¹⁸ O	4167.705	0.120	4050.463	0.119
H ₂ CC ¹³ CO	4373.222	0.236	4244.680	0.253
H ₂ ¹³ CCCO	4255.756	0.051	4133.097	0.052
(E)-HDCCCO	4124.842	-0.084	4000.933	0.139
(Z)-HDCCCO	4227.807	0.146	4059.367	-0.161

tunnelling in the ground state, so that the two monodeuterio forms interconvert extremely slowly and are essentially distinct species.⁶

Finally it should be noted that not all of the internal angular momentum contribution to C originating from ν_{12} has been removed. That part that is attributable to hypothetical oscillations in one well of the double-minimum potential remains, in the same way that internal angular momentum makes some small contribution to the effective rotational constants in most semirigid molecules.

Molecular Structure. The derived rotational constants enable substitution coordinates to be calculated for all but the atom C₂. Although the A rotational constant is accurately known only for the main species, the Kraitchman⁷ equations can be rearranged for planar molecules by making the assumption that the inertial defect ($\Delta = I_c - I_b - I_a$), which is zero for a rigid planar body, is unchanged on isotopic substitution. This leads to the expressions

$$|r_a| = \left[\frac{\Delta I_b}{\mu} \left(1 - \frac{\Delta I_b - \Delta I_c}{I_b - I_a} \right) \right]^{1/2} \quad (1)$$

$$|r_b| = \left[\frac{\Delta I_c - \Delta I_b}{\mu} \left(1 - \frac{\Delta I_c}{I_b - I_a} \right) \right]^{1/2}$$

where

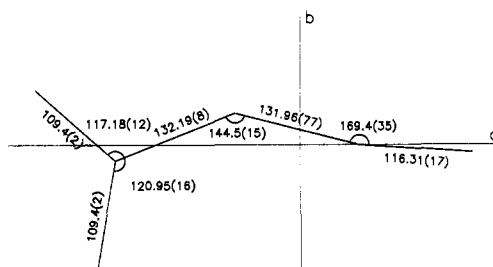
$$\mu = M\Delta m / (M + \Delta m)$$

for the coordinates of the nuclei. The substitution coordinates so obtained are given in Table III. The C₁ nucleus lies almost exactly on the a -principal axis, making the sign for r_b uncertain. The position of the C₂ nucleus could be determined by using the first moment equations:

$$\sum_{\text{nuclei}} m_i r_{ai} = 0 \quad (2)$$

However, the sign ambiguity of r_b (C₁) contributes directly to the uncertainty of the C₂ coordinate making this an unsatisfactory solution.

A better approach is to find an r_0 structure (via a least-squares fit of the molecular structure to the B and corrected C rotational constants) that is optimized for consistency with the well-determined r_s coordinates. The r_0 method in isolation suffers from strong correlations between a group of structural parameters comprising the heavy-atom chain angles and the distances C₁O

**Figure 1.** The structure of propadienone. The internuclear distances are given in pm. Uncertainties are shown in parentheses in units of the least significant digit of the parameter. Outside the indicated uncertainty ranges, the coordinates of the C₁ and O nuclei were found to be clearly inconsistent (>2-pm difference) with the corresponding coordinates derived by the isotopic substitution method. (See text for details.)

and C₁C₂. This is probably attributable to the proximity of C₁ to the a axis. This correlation, which causes large apparent uncertainties in the structural parameters, can be removed by using a constrained structure in which the angle $\angle C_1C_2C_3$ is held constant in the least-squares fit. The best-fit value of this angle was found by repeating the least-squares calculation for a series of assumed values of this angle. It was found that the best fit r_b coordinates, particularly of the C₁ and O nuclei, depart considerably from the r_s values if $\angle C_1C_2C_3$ is varied far from 144.5°—a bend of 35.5° away from linearity. The r_0 coordinates with $\angle C_1C_2C_3$ at this angle and 1.5° either side are included in Table III. In this range the root mean square deviation of the fit does not vary significantly from the minimum value of 0.156 MHz which occurs for a bend of 145.9°.

The experimentally determined structure is illustrated in Figure 1. It is an r_0 structure, but the uncertainties in the structural parameters, rather than being those derived from the residuals in the least-squares method, cover the range of values in Table III. Outside this range the coordinates of the C₁ and O nuclei are clearly inconsistent (>2-pm difference) with the substitution coordinates. The rotational constants predicted by the structure are compared with the experimentally determined values in Table IV.

Discussion

This method of deriving the molecular structure involving both r_s and r_0 formulae is not entirely satisfactory. A better solution would clearly be to substitute at the C₂ position and then to use the first moment eq 2 to decide on the sign of r_b for the atom C₁, thus providing a complete substitution structure. Nevertheless, the most interesting aspect of the structure of propadienone—the kinked heavy-atom chain—is shown to have a zigzag conformation, bent mainly at the C₂ atom by $\sim 35.5^\circ$, but with a considerable bend of 11° at the C₁ atom as well.

The structure of propadienone has aroused interest particularly among quantum chemists since it is apparently the first example in which the inclusion of electron correlation terms in the Hamiltonian is vital to the satisfactory prediction of the observed symmetry point group. Fully optimized single-configuration Hartree-Fock calculations employing sophisticated Gaussian basis

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(7) Kraitchman, J. Am. J. Phys. 1953, 21, 17-24.

sets and including polarization functions, previously considered to be infallible in the prediction of the qualitative aspects of molecular structure, fail to produce any deviation from linearity in the heavy-atom chain.^{8,9} Following the publication of the experimental evidence that propadienone has a C_s rather than C_{2v} structure, quantum chemists have shown that when electron correlation is included either by perturbation¹⁰ techniques or in multi-configurational-SCF calculations^{11,12} then the predicted energy minimum for propadienone occurs for an unsymmetrical structure similar to the experimentally determined one reported here. Brown and Dittman¹¹ showed that the kinked geometry is primarily attributable to a contribution to the ground state from the lowest energy doubly excited electronic configuration. Farnell and Radom¹⁰ have pointed out that the flatness of the ν_{12} potential function at the Hartree-Fock level makes it feasible for any conflicting influence arising from electron correlation to manifest itself in a resultant double-minimum potential function.

Taylor¹² employed the recently developed CASSCF method with an augmented double- ζ plus polarization basis set to obtain a fully optimized equilibrium structure. The heavy-atom angles were predicted to be $\angle C_1C_2C_3 = 139.5^\circ$ and $\angle OC_1C_2 = 165.5^\circ$.

A number of ketene homologues and related molecules have been studied by spectroscopic methods, and it appears that unusually flat potentials for bending vibrations analogous to the ν_{12} mode of propadienone are the norm rather than exceptional within this group; the methylene wag force constants for ketene ($C-H_2:C:O$)¹³ and diazomethane ($CH_2:N:N$)^{14,15} are respectively one-third and one-fifth of that for ethylene; the ν_{15} (out of

heavy-atom plane) mode of cyclopropylidene methanone ($\overline{CH_2 \cdot CH_2 \cdot C:C:O}$)¹⁶ and the ν_7 mode of carbon suboxide ($O:C:C:O$)¹⁷ each have very shallow potentials with small central barriers rising to the vicinity of the vibrational ground-state energy; the ν_{15} mode of butatrienone ($CH_2:C:C:O$)¹⁸ has a shallow single minimum potential.

In each of these molecules, the ease of deformation may be attributable qualitatively to the influence of a canonical form containing $=C_2-C_1 \equiv O^+$ or in the case of diazomethane the isoelectronic $=C-N^+ \equiv N$ analogous to II for propadienone. The influence appears usually merely to flatten the bending potential without distorting the equilibrium structure, but in a few cases, stabilization of the bent form may be sufficient to lower the symmetry of the equilibrium structure. To date, propadienone is the only experimentally observed example for which substantial potential minima (in comparison with zero-point vibrational energy) develop for the deformed structure. From the viewpoint of ab initio molecular orbital calculations, propadienone is a unique case in which the inclusion of electron correlation is essential for the correct prediction of the symmetry of the equilibrium structure.

Acknowledgment. This work was supported by funding from the Australian Research Grants Scheme.

Registry No. $H_2CCC^{18}O$, 79048-71-8; $H_2CC^{13}CO$, 96445-82-8; $H_2^{13}CCCO$, 79048-72-9; $HDCCCO$, 64918-70-3; H_2CCCO , 61244-93-7.

Supplementary Material Available: Tables of ground-state rotational transitions for isotopic variants of propadienone and correlation matrices from the least-squares fit (5 pages). Ordering information is given on any current masthead page.

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The Microwave Spectrum and Structure of Tricarbon Monoxide

Ronald D. Brown,* Peter D. Godfrey, Patricia S. Elmes, Martin Rodler, and Leslie M. Tack

Contribution from the Department of Chemistry, Monash University, Clayton, Victoria, Australia 3168. Received January 18, 1985

Abstract: The microwave spectra of tricarbon monoxide isotopically substituted with ^{13}C or ^{18}O at each of its four atoms in turn are reported. From the derived rotational constants the full substitution geometry of this linear molecule is derived, viz., $r_s(C_1O) = 115.0$ pm, $r_s(C_1C_2) = 130.6$ pm, $r_s(C_2C_3) = 125.4$ pm. Discrepancies with ab initio molecular orbital calculations (MP3/6-31G*) are somewhat larger than usual, perhaps because of the effect of a low-frequency bending vibration. From observations of l -doubling transitions we estimate the bending frequency to be about 150 cm^{-1} , reasonably near the theoretical prediction of 200 cm^{-1} . The oxide was generated from a more convenient precursor—fumaroyl dichloride. The preparations of required isotopically enriched versions of this compound are described.

We have recently reported the generation of C_3O by pyrolysis, its identification being based on observations of six lines in the microwave spectrum of the common isotopic species,¹ the line frequencies being in close accord with predictions based on ab initio molecular orbital calculations on the properties of C_3O .²

We now report a more extensive study of the microwave spectrum of C_3O , including all monoisotopically substituted versions of the molecule. We also describe an alternative pyrolysis for generating C_3O from fumaroyl dichloride ((*E*)-2-butenediol dichloride) that has proved more convenient both for isotopic synthesis and for spectroscopic observations.

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