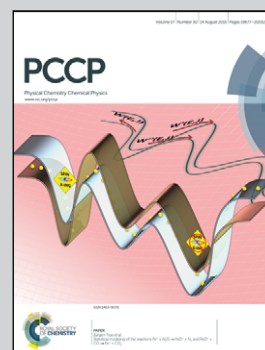**Showcasing research from an international collaboration of the laboratories of J.-U. Grabow, E. Cocinero and D. McNaughton.**

Title: Conformational steering in dicarboxy acids: the native structure of succinic acid

The torsional freedom of the carbon backbone and hydroxyl groups of succinic acid, an important platform chemical finding numerous industrial applications as well as being the focus of considerable research in atmospheric science, is elucidated. The question of the potential presence of numerous conformers is answered by an unambiguous identification of the structural and molecular properties using microwave and millimeter wave spectroscopy. The precise spectroscopic data provides evidence that the anomalous tendency of "folding the methylene unit" is favoured.

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Conformational steering in dicarboxy acids: the native structure of succinic acid†‡

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Succinic acid, a dicarboxylic acid molecule, has been investigated spectroscopically with computational support to elucidate the complex aspects of its conformational composition. Due to the torsional freedom of the carbon backbone and hydroxy groups, a large number of potentially plausible conformers can be generated with an indication that the *gauche* conformer is favored over the *trans* form. The microwave and millimeter wave spectra have been analyzed and accurate spectroscopic constants have been derived that correlate best with those of the lowest energy *gauche* conformer. For an unambiguous conformational identification measurements were extended to the monosubstituted isotopologues, precisely determining the structural properties. Besides bond distances and angles, particularly the dihedral angle has been determined to be 67.76(11)°, confirming the anomalous tendency of the methylene units to favor *gauche* conformers when a short aliphatic segment is placed between two carbonyl groups.

Introduction

Succinic acid, historically known as spirit of amber, is an important platform chemical that finds numerous industrial applications[1–3] *e.g.* as an ingredient to stimulate animal and plant growth, an additive in food and pharmaceutical products, surfactants, detergents and as a feedstock chemical for the production of polyamides, polyesters and polyester amides as well as biodegradable plastics, with a global production of ~50 000 tons per year.[4] The US Department of Energy identifies succinic acid as one of the top 10 bio-based products with research needs[5] and its importance in the development of sustainable chemistry. Being a metabolite in the tricarboxylic acid cycle of several anaerobic and facultative microorganisms, succinic acid can be produced by fermentation of mixed sugars as renewable carbon sources. In addition, succinic acid is one of the few dicarboxylic acids present in the Earth's troposphere,[6] forming part of the organic matter that is found in continental

and marine aerosols. Organic acids have been the focus of considerable research in atmospheric science in the last few years, as the organic fraction can affect the properties of atmospheric aerosol particles such as light scattering, hygroscopicity, phase transition, solubility or chemical reactivity.[7] Carboxylic acids are also pivotal compounds in the nucleation processes of atmospheric aerosols, due to their ability to form stable heterodimers with other molecules *via* hydrogen bonding, forming the so-called critical nucleus of the aerosol.[8–14] Moreover, carboxylic acid molecules can be considered as building blocks that are present in several biological systems, where they play key roles because the acid groups can participate in intermolecular hydrogen bonding.[15] Thus characterizing the conformations and the molecular potential energy surface of isolated acid molecules as well as establishing the role played by hydrogen bonding can help in providing a better understanding of molecular recognition and self-assembly processes.[16]

Succinic acid can display a rich variety of conformational possibilities (Fig. 1), due to the torsional flexibility of the carbon chain and the C–O bonds that altogether can generate $2 \times 3 \times 3 \times 3 \times 2 = 108$ plausible conformers. This number is reduced when a variety of effects are considered, such as the so-called "folding of methylene units", the more general "*gauche* effect",[17,18] the possibility of formation of hydrogen bonds and the *Z/E* (*cis/trans*) arrangements of each carboxylic group. Of particular importance is the folding of methylene units,[19] the apparently anomalous tendency of the methylene units to favour *gauche* conformers when a short aliphatic
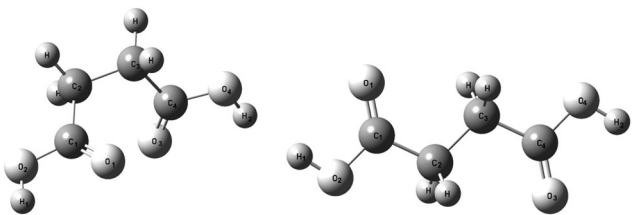
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Fig. 1 Conformational variability of the succinic acid molecule. Conformers are named by a series of five letters (E/Z)(g/c/t)(g/t)(g/c/t)(E/Z), where the first, second, third, fourth and fifth letters refer to the dihedral angles H1–O2–C1–O1, O1–C1–C2–C3, C1–C2–C3–C4, C2–C3–C4–O3 and O3–C4–O4–H2, respectively. For the terminal acid groups the E/Z nomenclature is used, whereas g, c and t stand for *gauche* (~60°), *cis* (~0°) and *trans* (~180°). In the figure the conformers ZcgcZ and ZctcZ are displayed.

segment is placed between two carbonyl groups. This phenomenon has been observed in several di-functional molecules, and also in aqueous succinic acid. In addition, succinic acid presents two diprotic groups which could stabilize some conformers *via* hydrogen bonds. Moreover, the E/Z-possibilities of each acid group determine the likelihood of hydrogen bond formation.[20]
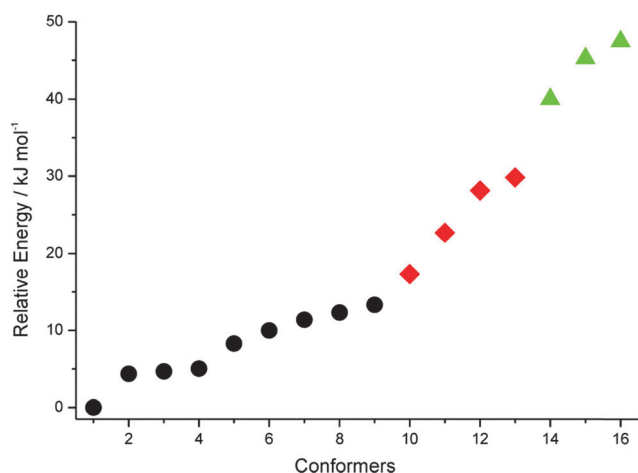
Fig. 2 Predicted energy (zero point corrected) for the 16 lowest-lying energy conformers (50 kJ mol^{-1}) of succinic acid at the MP2/6-311++G(d,p) level of theory. The circle indicates a ZZ configuration, the rhombus shows a ZE or EZ arrangement and the triangle shows an EE configuration of the carboxylic groups.
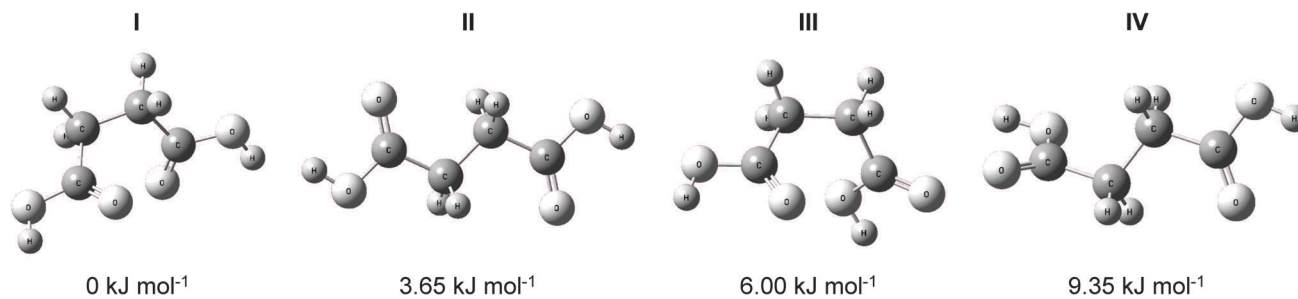
Optimized structures and relative energies of conformers of succinic acid in the gas phase have been reported using calculations at the MP2/6-311+G(d,p)//HF/6-31G(d)[21] and DFT-B3LYP/6-31+G(d,p) levels,[22] although they are outdated now.[23] For this reason our experiment has been supplemented with theoretical calculations intended to test the accuracy of different methods and basis sets. Previous neutron diffraction data for crystalline succinic acid are available[24] and show that the molecule is essentially planar and forms linear chains *via* hydrogen bonds in the crystal. In the presence of crystal lattice strain, it assumes a *trans* conformation about the central C2–C3 bond, in contrast to the *gauche* skeleton predicted by quantum calculations of the isolated molecule. Similar results have been provided by X-ray diffraction studies,[25,26] reporting that the carbon backbone is planar, and the carboxylic groups are strongly bonded by O–H···O intermolecular hydrogen bonds, as well as by C–H···O interchain interactions. NMR studies[27] have shown that neutral succinic acid in water exists mainly as the *gauche* conformer, even though extensive hydrogen bonding with water would be expected to favour different structures.[28] This effect is also related to the more general anomeric effect observed in carbohydrate rings.[29] The only gas phase study of succinic acid so far has been carried out by electron diffraction.[23] Measurements at 445 K indicated that succinic acid exists as a mixture of mostly four conformers – two *gauche* conformers (ZcgcZ and ZcgtZ) that are slightly dominant (55%) relative to the ZctcZ and ZgtcZ *trans* conformers (45% in total). Because experimental studies on the structure and internal dynamics of gaseous succinic acid are limited, further exploration of this molecule in search of a more precise conformational characterization is needed. The ideal conditions for the study of the former issues are achieved by preparing isolated molecules in the gas phase, where the influence of surrounding molecules of the same species or solvent molecules is absent. Pure rotational spectroscopy in the microwave region in supersonic expansions is a very high resolution technique and to date has been the most powerful tool that allows precise structure determination of gas-phase molecules in their ground electronic state. By combining data from rotational transitions belonging to different isotopologues, precise geometrical parameters can be derived. Different conformers of a given species can be unambiguously discriminated in their pure rotational spectra by consideration of the resultant values of their rotational constants, any hyperfine structure and the relative

Fig. 3 Four lowest energy conformers of succinic acid, ZcgcZ, ZctcZ, ZcgtZ, ZgtcZ respectively. The relative energies are zero point corrected at the MP2/cc-pVTZ level of theory.

| I | II | III | IV |
| 0 kJ mol^{-1} | 3.65 kJ mol^{-1} | 6.00 kJ mol^{-1} | 9.35 kJ mol^{-1} |

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intensities of transitions, which depend on dipole moment components. Expansion of the sample in a supersonic jet is accompanied by relaxation of the population from ro-vibrationally excited states to the lowest lying rotational levels, thus reducing the number of observed transitions and simplifying the spectral assignment. Also the experimentally obtained rotational constants can be directly compared with the *ab initio* calculated values so that the adequacy of electronic structure calculation methods can be assessed. In the present work the conformational landscape of succinic acid has been studied in the collision-free environment of a supersonic jet by combining the results obtained from three different spectrometers operating in the cm- and mm-wave regions. Measurements in the two microwave frequency bands provide essentially complementary information. Spectra in the higher frequency region, recorded using a Stark-modulated absorption spectrometer, provide a rapid and efficient panoramic overview of the spectrum at limited resolution, assisting in the recognition of any lines due to impurities and leading to the calculation of accurate molecular rotational constants which convey information on the location of the potential energy surface minima.

In contrast, lower frequency but much higher resolution spectra, recorded using Fourier transform microwave spectrometers, can de-correlate rotational and very accurate centrifugal distortion constants which relate to the curvature of the potential energy surface about the minima. Additionally, they may permit the measurement of nuclear quadrupole hyperfine coupling constants, which are dependent on details of the molecular electron distribution, if isotopologues with quadrupolar nuclei are available. The analysis of all ^{13}C, [18]O and D–(O) substituted isotopologues has been carried out in order to determine the effective (r_0)[30] and substitution (r_s) structures.[31]

Results and discussion

The conformational variability of succinic acid arises from a variety of concurrent effects. In consequence, a large number of possible optimized structures (Fig. 2) and relative energies had to be predicted and evaluated for conclusiveness. Therefore theoretical methods included MP2, B3LYP and Truhlar's dispersion-corrected M06-2X functional, all using a widely used 6-311++G(d,p) basis set and also using the larger cc-pVTZ basis set.

Notably, none of the four lowest-lying energy conformers (Fig. 3 and Table 1) are predicted to be stabilized by a hydrogen bond (HB) between the hydrogen of one carboxylic group and the oxygen of the other carboxylic group, which sterically would require an *E* configuration significantly higher in energy. Thus the theoretical results suggest that the stabilization achieved by an intramolecular HB is not sufficient to sacrifice the most stable *Z* configuration of the carboxylic groups. The difference between *E* and *Z* rotamers in formic acid was attributed to intramolecular hydrogen bonding by Hocking[32] and empirically corrected by Császár,[20] who measured the energy difference to be 17.2(3) kJ mol⁻¹.

Once a large repertoire of plausible structures was available, we initiated the scan of the microwave and millimeter wave

Table 1 Spectroscopic parameters (in Watson's S reduction), dipole moment components and relative energies of the four lowest-energy conformers of succinic acid calculated using the 6-311++G(d,p) basis set using different methods and the cc-pVTZ basis set using MP2 method

| | I | | | | II | | | | III | | | | IV | | | |
| | 6-311++G(d,p) | | | cc-pVTZ | 6-311++G(d,p) | | | cc-pVTZ | 6-311++G(d,p) | | | cc-pVTZ | 6-311++G(d,p) | | | cc-pVTZ |
	MP2	M06-2X	B3LYP	MP2	MP2	M06-2X	B3LYP	MP2	MP2	M06-2X	B3LYP	MP2	MP2	M06-2X	B3LYP	MP2
A/MHz	4245.5	4360.5	4334.0	4276.8	5493.7	5602.7	5542.4	5520.1	4057.5	4190.8	4183.6	4099.3	5211.3	5388.7	5311.7	5459.5
B/MHz	1229.0	1227.5	1145.0	1224.7	926.3	934.0	919.5	934.9	1284.1	1281.4	1195.6	1278.1	911.0	921.8	902.6	946.1
C/MHz	1202.0	1195.2	1141.0	1200.9	806.4	808.3	796.2	807.2	1239.7	1237.4	1176.7	1241.0	860.5	850.7	843.4	814.2
D_J/kHz	0.60	0.47	0.59	0.61	0.05	0.03	0.03	0.03	0.57	0.47	0.57	0.60	0.09	0.07	0.09	0.03
D_K/kHz	9.06	8.34	10.76	9.72	1.13	1.06	1.08	1.08	7.56	7.55	8.98	8.39	2.53	3.00	3.61	10.59
D_{JK}/kHz	−1.38	−1.67	−1.65	−1.76	0.25	0.17	0.18	0.18	−1.42	−1.68	−1.08	−1.70	1.74	1.03	2.06	1.64
d_1/Hz	−36.00	−33.60	−49.90	−38.45	−4.31	−4.37	−4.37	−4.51	−28.20	−23.70	−49.40	−35.28	12.50	10.40	17.4	−4.84
d_2/Hz	5.96	−1.63	−0.90	3.00	−10.90	−0.43	−0.42	−0.46	1.43	0.29	−1.84	0.97	−22.80	−15.40	−26.8	−0.27
$\lvert\mu_a\rvert$/D	0.0	0.0	0.0	0.0	0.4	0.0	0.0	0.0	0.8	2.0	1.9	1.9	0.7	0.9	0.9	1.0
$\lvert\mu_b\rvert$/D	1.5	1.8	1.8	1.7	0.0	0.0	0.0	0.0	2.0	1.7	2.0	2.2	1.7	2.2	2.2	2.5
$\lvert\mu_c\rvert$/D	0.0	0.0	0.2	0.0	0.4	0.0	0.0	0.0	1.8	1.7	1.4	0.8	1.0	0.2	0.2	0.0
μ_{TOT}/D	1.5	1.8	1.8	1.7	4.6	2.3	0.1	3.4	2.8	3.1	3.1	3.0	2.1	2.5	2.4	2.7
$\Delta E + ZPVE$/kJ mol⁻¹	0.0	0.0	0.0	0.0	4.6	2.3	0.1	3.4	5.0	5.4	6.1	5.8	8.3	8.5	5.8	10.1
ΔG/kJ mol⁻¹	0.0	0.0	0.0	0.0	1.3	−2.6	3.6	0.8	5.9	5.7	6.2	6.3	6.1	5.7	3.5	12.9

spectra by heating the sample at 180 °C. The archived spectrum was denser than expected and reheating the sample increased the intensity of several unassigned transitions. These transitions were identified in a second experiment to belong to succinic anhydride, by measuring anhydride alone. Excluding these lines from the fit, succinic acid was identified. Alternative spectra of succinic acid obtained by the UV laser vaporization method produced only the lines of succinic acid, thus avoiding the formation of any undesirable compound.

The measurements of Hannover and Bilbao (7–18 GHz) result in a set of ^{b}Q-branch ($J \leftarrow J$) and ^{b}R-branch ($J + 1 \leftarrow J$) transitions with low angular momentum quantum numbers in the range of J = 2–10. Fig. 4 shows a section of the spectrum where a Q-branch pattern was identified for succinic acid. These measurements were extended to higher energy levels, J up to 28, by recording the spectra in the mm-wave region. All experimental transitions of succinic acid are limited to μ_b selection rules and are collected in the ESI.‡ a- and c-type
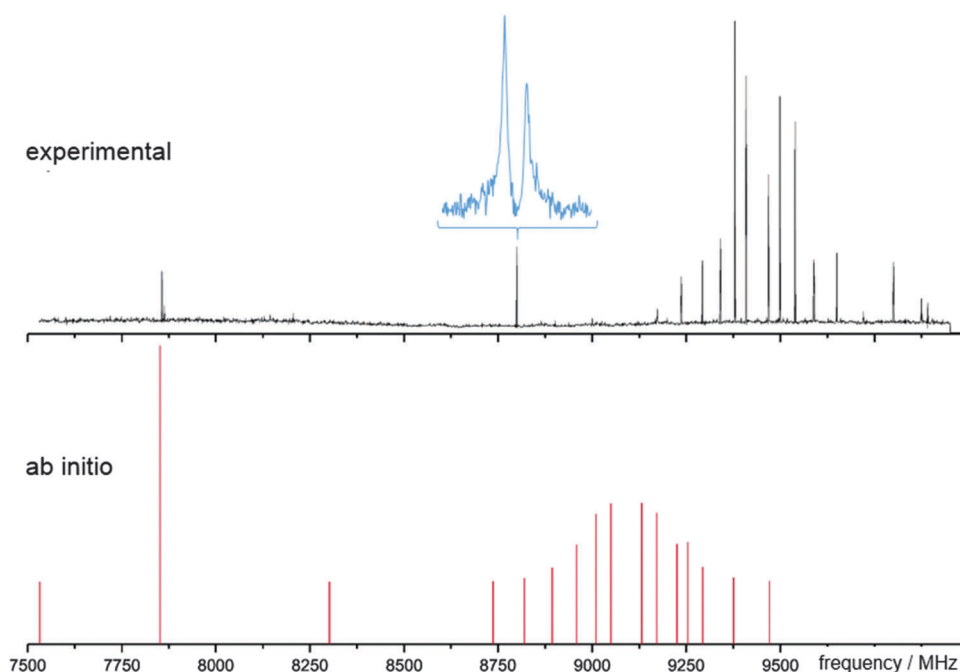

Fig. 4 A section of the jet-cooled cm-wave rotational spectrum of succinic acid *via* laser ablation (upper trace) compared to the *ab initio* simulation (lower trace) at MP2/6-311++G(d,p). A typical ^{b}Q-branch pattern is observed in the spectrum. Image enlargement is the amplitude spectrum of the $5_{15} \leftarrow 4_{04}$ (J_{K^+,K^-}) transition in the cm-wave region. The doublet arises from the Doppler effect of the jet-expansion coaxial to the propagation of the electromagnetic wave.

Table 2 Rotational parameters of succinic acid and comparison with theoretical predictions for the most stable conformation

	Experiment	MP2/ 6-311++G(d,p)	B3LYP/ 6-311++G(d,p)	M06-2X/ 6-311++G(d,p)	MP2/ cc-pVTZ	B3LYP/ cc-pVTZ	M06-2X/ cc-pVTZ	MP2/aug-cc-pVTZ	B3LYP/aug-cc-pVTZ	M06-2X/aug-cc-pVTZ
A^a/MHz	4331.32649(12)	4245.5	4334.0	4360.5	4299.4	4368.8	4371.8	4276.8	4349.5	4351.1
B/MHz	1194.975395(72)	1229.0	1145.0	1227.5	1223.0	1146.1	1226.1	1224.7	1144.8	1227.0
C/MHz	1174.979636(67)	1202.0	1141.0	1195.2	1198.9	1141.9	1196.9	1200.9	1142.0	1198.8
D_J/kHz	0.60057(61)	0.60	0.47	0.59	0.58	0.59	0.51	0.61	0.61	0.53
D_{JK}/kHz	−2.0175(21)	−1.38	−1.65	−1.67	−1.74	−1.69	−1.96	−1.77	−1.76	−2.01
D_K/kHz	10.2085(65)	9.06	10.76	8.34	9.66	10.89	9.11	9.73	11.14	9.37
d_1/Hz	−45.75(34)	−36.00	−49.90	−33.60	−32.67	−51.00	−36.6	−38.45	−50.98	−38.08
d_2/Hz	−6.2(16)	5.96	−1.63	−0.90	−2.85	−1.86	−1.15	3.00	−1.09	−0.62
$|\mu_a|^b$/D	—	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
$|\mu_b|$/D	—	1.5	1.8	1.8	1.5	1.7	1.7	1.7	1.8	1.8
$|\mu_c|$/D	—	0.0	0.0	0.2	0.0	0.0	0.0	0.0	0.0	0.0
N^c	71									
rms res/kHz	0.98									

^{a} Rotational constants A, B, C; Watson's S-reduction quartic centrifugal distortion constants D_J, D_{JK}, D_K, d_1, d_2. ^{b} Dipole moment components (μ_a, μ_b, μ_c in debye units, 1D ≈ 3.336×10^{-30} C m). ^{c} Number of transitions (N) and rms deviation of the fit.

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transitions could not be observed in the experiment. All other observed transitions were assigned to the anhydride, in contrast to the gas electron diffraction (GED) study which did not consider the presence of anhydride.[23] Conformer II might be present but remains undetectable because of its largely missing dipole moment, providing no evidence of a second conformer under the experimental conditions.

The experimental data set allowed us to determine the rotational constants (A, B, C) and all Watson S-reduced quartic centrifugal distortion parameters (D_J, D_{JK}, D_K, d_1, d_2). A first comparison of the experimentally determined parameters with the theoretical predictions (Table 2) immediately established that the observed spectrum is compatible with the rotational constants of either structure I or III in Table 1, which correspond to *gauche* forms of succinic acid. *trans* structures from Table 1 were excluded, as their *ab initio* rotational constants give errors in the 23–28% range, *vs.* 1–6% for the *gauche* forms. Whilst at the vaporization temperature of 180 °C the population of the *trans* species would be 23% of the total, under the post-expansion conditions of the supersonic jet this fraction would be considerably less. Regardless, the *trans* configuration (C_{2h} symmetry) could be omitted for the spectral prediction due to its zero dipole moment.

The rotational parameters predicted for conformer I show a smaller deviation from the experimentally determined values
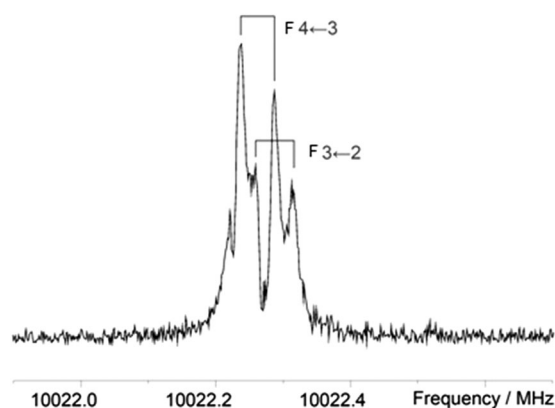
(deviations for A–C range from 1.7 to 2.4%) than those predicted for conformer III (1.2–6.4%), which is the second lowest energy conformer having a nonzero dipole moment. Additionally, the sole observation of a b-type spectrum is only consistent with conformer I, as conformer III would also give a- and c-type spectra. Conformer III is predicted at the MP2/cc-pTVZ level to be 6 kJ mol^{-1} higher in energy with considerably less population after conformational relaxation in the rotationally cold (2 K) jet during the supersonic expansion, even if the sample is heated to 180 °C to seed Ne. Thus it is unlikely that we can observe conformer III under our experimental conditions. These facts led us to confidently assign the observed species to conformer I.

For an unambiguous conformational identification, the experimental measurements were extended to other mono-substituted isotopic species in natural abundance. The rotational spectra of both ^{13}C isotopologues (1.1%) were first detected and analyzed including the centrifugal distortion parameters. Later on, the measurements were extended to the weaker ^{18}O species (~0.2%), confirming the high sensitivity of the FTMW and mm-wave techniques. Finally the deuteron hydroxy group (0.015%) was measured by treating normal succinic acid with D$_2$O, which shows resolvable hyperfine effects (Fig. 5), from which the diagonal elements of the nuclear quadrupole coupling tensor χ_{aa}, χ_{bb} and χ_{cc} could be determined. As a consequence of the C_2 symmetry of the molecule, ^{13}C (positions 1/4 and 2/3), ^{18}O (positions 1/3 and 2/4) and D (position 1/2) gave rise to lines of double intensity. The rotational parameters of all the measured isotopologues are shown in Table 3.

Fig. 5 A typical transition ($J = 3_{13} \leftarrow 2_{02}$) of the deuterated succinic acid where hyperfine components are due to ^{2}H nuclear quadrupole coupling to the molecular rotation.

Table 4 Substitution coordinates of succinic acid (Å)

Atom	a	b	c
C(1)	−1.51562(4)	[0.0][a]	0.18616(29)
C(2)	−0.68375(5)	1.11317(3)	−0.30168(12)
C(3)	0.68375(5)	1.11317(3)	0.30168(12)
C(4)	1.51562(4)	[0.0][a]	−0.18616(29)
O(1)	−1.22347(35)	−0.77276(43)	1.10494(50)
O(2)	−2.67128(3)	−0.16643(49)	−0.50690(17)
O(3)	1.22347(35)	−0.77276(43)	−1.10494(50)
O(4)	2.67128(3)	−0.16643(49)	0.50690(17)
H(1)	−3.13499(3)	−0.92066(9)	−0.15677(58)
H(2)	3.13499(3)	−0.92066(9)	0.15677(58)

[a] The value held constant in the fit.

Table 3 Observed molecular constants[a] of succinic acid isotopologues

	^{13}C$_2$/^{13}C$_3$	^{13}C$_1$/^{13}C$_4$	^{18}O$_1$/^{18}O$_3$	^{18}O$_2$/^{18}O$_4$	D$_1$/D$_2$[b]
A/MHz	4282.82506(66)	4330.05371(72)	4203.47341(201)	4311.49095(274)	4300.20361(107)
B/MHz	1193.43963(40)	1188.45630(52)	1181.19419(126)	1155.18376(132)	1167.72268(58)
C/MHz	1170.322984(265)	1168.768636(264)	1162.59252(91)	1137.57417(106)	1146.53209(60)
D_J/kHz	0.5913(54)	0.6003(78)	0.6081(178)	0.5689(188)	0.5771(52)
D_{JK}/kHz	−2.0127(315)	−2.048(36)	−1.832(87)	−2.042(90)	−2.148(39)
D_K/kHz	10.003(51)	10.232(48)	9.250(111)	10.426(113)	10.593(64)
d_1/kHz	−0.04575[c]	−0.04575[c]	−0.04575[c]	−0.04575[c]	−0.03985(282)
d_2/kHz	−0.000616[c]	−0.000616[c]	−0.000616[c]	−0.000616[c]	−0.000616[c]

[a] Rotational constants A, B, C; Watson's S-reduction quartic centrifugal distortion constants D_J, D_{JK}, D_K, d_1, d_2. [b] Nuclear quadrupole coupling constants $\chi_{aa} = -0.0728(207)$ MHz, $\chi_{bb} - \chi_{cc} = 0.0291(58)$ MHz. [c] Held at the value of the main isotopologue.
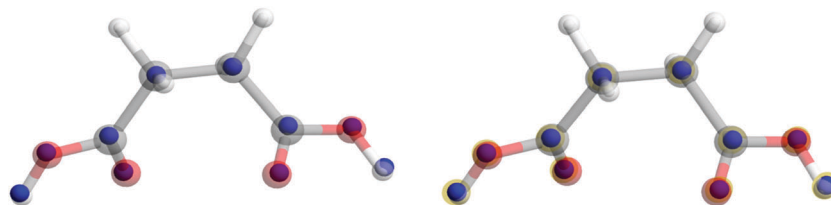
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Fig. 6 Substitution (r_s, left) and effective (r_0, right) structures superimposed on the *ab initio* (r_e) structures of succinic acid (see Table 5). The molecular framework is the theoretical structure, while the smaller, darker spheres are located at the experimentally determined atom positions.

Table 5 Bond lengths (Å), angles < (deg) and dihedral angles τ (deg) of the substitution and effective structures of succinic acid and quantum chemical prediction for conformer I

Parameter	r_s	r_0	r_e
C(2)−C(3)	1.4947(80)	1.5220(87)	1.5135
C(3)−C(4)	1.4728(78)	1.5066(59)	1.5043
C(4)−O(3)	1.2355(93)	1.2014(32)	1.2092
C(4)−O(4)	1.3578(81)	1.3538(21)	1.3509
O(4)−H(2)	0.953(13)	0.9691(79)	0.9689
<C(1)−C(2)−C(3)	112.52(69)	111.93(14)	111.06
<C(2)−C(1)−O(1)	125.83(64)	125.38(30)	125.44
<O(1)−C(1)−O(2)	120.27(72)	123.12(45)	123.09
<C(1)−O(2)−H(1)	109.0(1.2)	106.04(74)	105.53
<C(2)−C(1)−O(2)	113.8(1.0)	111.55(30)	111.45
τC(1)−C(2)−C(3)−C(4)	−70.19(1.4)	−67.76(11)	−67.06
τO(2)−C(1)−C(2)−C(3)	169.2(1.1)	169.34(27)	169.66
τH(1)−O(2)−C(1)−C(2)	177.9(1.4)	179.18(33)	179.22

Table 6 Dihedral angles (deg) of 1,2-ethane derivatives

Molecule	Dihedral angle
Ethyl cyanide[35]	59.95(18)
Succinonitrile[36]	65.9(23)
Succinic acid [this work]	67.76(11)
1,2-Dichloroethane[37]	68.1(7)
1,2-Difluororoethane[38]	71(3)

with that of several 1,2-ethane derivatives, XCH_2CH_2Y. As seen in Table 6, the pairs of electronegative substituents increase the dihedral angle compared to the 60° expected for ethane itself, enabling 1,2-difluoroethane (71°) and 1,2-dichloroethane (68.1°) to have larger dihedral angles. This trend is also in line with succinonitrile (65.9°), the nitrile of succinic acid, but is in contrast to ethyl cyanide (59.95°) where, in the presence of a single substituent, the dihedral angle assumes that of ethane itself.

The molecular structure of succinic acid was derived from a set of 18 rotational constants of a single detected conformation. A vibrational ground-state effective structure (r_0) was determined by nonlinear least-squares fitting. Additionally, a substitution structure (r_s), which requires isotopic substitution for each atomic position to be determined, was obtained (Table 4 and Fig. 6) using Kraitchman's equations[31] with the uncertainties estimated according to Costain's rule[33] using the software of Kisiel.[34] Structural details, such as bond lengths, angles and dihedral angles were derived for comparison with the r_0 structure, see Table 5. These structures are also compared with the near-equilibrium (r_e) *ab initio* structure at the MP2/cc-pVTZ level of theory. These parameters unambiguously confirm that the *gauche* structure I of succinic acid is the one observed in our experiments. The *ab initio* method MP2/cc-pVTZ is in excellent agreement with the experimental effective structure; all the bond lengths, angles and dihedral angles are closely reproduced. The discrepancy in comparison to the substitution structure is larger which can be rationalized from the C1 and C4 atoms being very close to b axis, hence increasing the experimental uncertainty in the determination of these positions. The most interesting parameters are the dihedral angles C1–C2–C3–C4 and O1–C1–C4–O3, determined to be 67.76(11)° and 74.60(11)° respectively, which quantitatively reflects the *gauche* conformation. This apparently anomalous tendency to favor a *gauche* form over a *trans* arrangement is the well-known "folding of methylene units" or "*gauche* effect" and was also observed in other XCH_2CH_2Y molecules and even in aqueous succinic acid. The dihedral angle of succinic acid can be compared

Conclusions

A conformational search using a number of basis sets located 16 conformers of succinic acid within 50 kJ mol^{-1} with the four lowest energies within 10 kJ mol^{-1}. All theoretical methods predict the *gauche* conformer I as the lowest energy structure. Indeed, under the conditions of the supersonic jet expansion, only lines belonging to this low energy conformer were observed experimentally. Whereas the conformer predicted as second lowest in energy has zero dipole moment and hence no rotational spectrum to confirm or rule-out its presence, the six polar conformers next in energy can be excluded from making a significant contribution to the composition of the jet as no spectral signatures have been found. From the remaining species only two more conformers carry no dipole moment. The others can be ruled out due to their missing spectra and higher energy. The analysis of the high-resolution microwave and millimetre-wave spectra of *gauche* succinic acid and its major substituted isotopologues provided not only very accurate spectroscopic constants but also allowed for the precise determination of effective ground-state and substitution experimental structures to gauge the theoretical predictions. The major bond lengths and bond angles are in accordance with those of the similar molecules, whilst the dihedral angle is shown by comparison with other substituted ethanes to be controlled by the repulsive nature of the substituents, here the carbonyl groups.

The experimental identification of the *gauche* conformer of succinic acid and its quantitative structural description are of pivotal importance in a detailed understanding of the mechanism of new particle formation in the Earth's atmosphere: the first step in generating the critical nucleus of the particle when organic acids are present involves the formation of hetero-dimers with other gaseous molecules in the troposphere, mainly sulfuric acid (widely known as one of the major atmospheric nucleating species).[14] In that way, succinic acid can form hydrogen bonds with sulfuric acid of the form $C=O\cdots H-O-S$ and $C-O-H\cdots O=S$. As a consequence, the precisely determined co-ordinates of succinic acid atoms (3D structure of the dominant monomer) map-out the location and orientation of intermolecular interactions that the dimer creates. From the energy differences between succinic acid conformers predicted *ab initio*, even at the rather high temperatures present at the planetary boundary layer (the lowest part of the atmosphere), with a typical value of 20 °C, the structure assigned as conformer I makes about 75% of the total population of succinic acid (with only the four lowest-energy conformers being of significant presence), which means that the *gauche* conformer will make the most important contribution to the sterical availability, therefore preconditioning the subsequent steps in particle formation and growth.

Experimental section

Experimental methods

The rotational spectrum of succinic acid was recorded using three spectrometers: the spectra in the cm-wave region (7–26 GHz) were obtained using two high-resolution pulsed supersonic jet-expansion Fourier transform microwave (FT-MW) spectrometers of Balle–Flygare-type[39] in Hannover (2–26 GHz)[40] and Bilbao (4–18 GHz),[41] both using the COBRA technique.[42] In the 48–70 GHz mm-wave region the spectra were recorded using a free-jet, Stark-modulated absorption spectrometer at Monash University, that has been modified with solid state sweep oscillator sources.[43] The three instruments have been described extensively;[40–43] therefore, only brief experimental details are given here. The solid sample was inserted inside a reservoir located at the nozzle exit and heated at 110–180 °C in the Hannover and Monash spectrometers. Extensive initial spectral searches encountered an unexpectedly dense spectrum. This anhydride spectrum was assigned along with the ^{13}C and ^{18}O isotopologues in natural abundance[44] in order to eliminate these lines for consideration of the acid. Subsequently the main isotopologue, all C-substituted isotopologues and all but one O-substituted isotopologue of succinic acid were recorded in natural abundance and identified. Alternatively, in the Bilbao spectrometer a solid rod target, compacted under pressure, was vaporized by an ultrafast Nd:YAG picosecond laser (355 nm, *ca.* ~5 mJ per pulse).[45] The UV laser vaporization system offered a complementary method to vaporize the sample avoiding decomposition products, identifying the missing O-substituted and D isotopologues. In Hannover and Bilbao, argon or neon at 3–6 bar was used as a carrier gas, creating a supersonic jet that was expanded along the axis of the evacuated Fabry–Perot resonators. Typically, short microwave pulses of 0.2–0.5 μs length (<10 mW) were used to polarize the sample. The resulting transient free-induction decay in the time domain was Fourier transformed to the frequency domain. The molecular resonances appear as a Doppler doublet (Fig. 4) because of the coaxial orientation (COBRA arrangement)[42] of the jet and resonator axes. The accuracy of frequency measurements is better than 3 kHz with experimental uncertainties of <500 Hz. In the mm-wave free-jet spectrometer the sample was entrained in a stream of argon at 0.3 bar and introduced between the Stark electrodes of the spectrometer *via* a 350 μm diameter pinhole nozzle held 10 °C above the vaporization temperature. Under these conditions the post-expansion rotational temperature was *ca.* 10 K. Electric fields up to 1600 V cm^{-1} between parallel plates separated *ca.* 3.5 cm were used for Stark modulation. A Lorentzian line shape function was fitted to each transition line profile exhibiting a typical full width half height (FWHH) of 100–200 kHz, leading to experimental line center-frequency uncertainties of 10 to 40 kHz.

Quantum-chemical calculations

Initial calculations using the MP2/cc-pVTZ levels of theory found 4 minimal energy conformers (Fig. 3), for which rotational constants, centrifugal distortion constants and dipole moments were calculated (Table 1). One of these conformers (II) has essentially zero dipole moment and another (IV) is quite high in energy and therefore they are not expected to appear in the spectrum. Thus, the initial analysis was started assuming that only lines from conformers I and III would appear in the spectrum, with conformer I expected to dominate.

For completeness, an exhaustive conformational search, in addition to that above, was performed to identify all possible conformers. The computational work was carried out in several steps. First, a comprehensive conformational search was accomplished using a fast molecular mechanics method (MMFFs[46]) and advanced Monte Carlo and large-scale low-mode conformational search algorithms. All structures (Fig. 2) in an energy window of 50 kJ mol^{-1} were later fully re-optimized using both *ab initio* (MP2) and density functional theory (DFT) methods, in the last case applying two different functionals (B3LYP and dispersion-corrected M06-2X) implemented in Gaussian 09.[47] A Pople 6-311++G(d,p) basis set was used in all cases (Table 1). Later, the global minimum was further re-investigated using DFT (B3LYP and M06-2X) and MP2 methods and triple-ξ Dunning's correlation consistent cc-pVTZ and aug-cc-pVTZ basis sets (Table 2). The calculation of the vibrational frequencies and centrifugal distortion constants used the harmonic approximation.

Acknowledgements

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