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To cite this version:

Christina Dindic, Wolfgang Stahl, Ha Vinh Lam Nguyen. 2-Propionylthiophene: planar, or not planar, that is the question. Physical Chemistry Chemical Physics, 2020, 22 (35), pp.19704-19712. 10.1039/D0CP02749A . hal-03182505

HAL Id: hal-03182505
https://hal.u-pec.fr/hal-03182505v1

Submitted on 26 Mar 2021

2-propionylthiophene: Planar, or not planar, that is the question

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Received 00th May 2020,
Accepted 00th May 2020

DOI: 10.1039/x0xx00000x

The long-standing ambiguity of the molecular planarity when an alkyl group is attached on a system with conjugated double bonds is a great challenge for both experiments and theory. This also holds for the case of 2-propionylthiophene (2PT) where a propionyl group is attached at the second position of the planar, aromatic thiophene ring. Results from quantum chemistry at the MP2 level of theory, showing that in the two conformers *syn*- and *anti*-2PT the ethyl group of the propionyl moiety is slightly tilted out of the thiophene ring plane, conflict with those from the other methods, stating that the ethyl group is in-plane with the thiophene ring. In the microwave spectrum, both *syn*- and *anti*-2PT were observed, and their geometry parameters such as the rotational and quartic centrifugal distortion constants were precisely determined. The experimental heavy atom skeleton obtained by isotopic substitutions revealed a tiny, but non-zero tilt angle of the ethyl group out of the thiophene plane, thereby convincingly confirming the non-planarity of 2-propionylthiophene. The results were further supported by internal defects calculated from the experimental rotational constants. Finally, splittings arising from the internal rotation of the terminal methyl group were analysed, yielding torsional barriers of 806.94(54) cm^{-1} and 864.5(88) cm^{-1} for the two observed conformers, respectively.

1 Introduction

The planarity of *gauche* 1,3-butadiene had remained ambiguous for decades because of controversial results from both experimental methods with IR, NMR, Raman and UV spectroscopy and theoretical studies until 2018, when Fourier transform microwave (FTMW) spectroscopy revealed its gas phase structure and gathered the conclusive evidence that *gauche* 1,3-butadiene is *not* planar. The tilt angle between two double bonds, determined with isotopic substitution, is 34°. Therefore, *gauche* 1,3-butadiene must first adopt a planar conformation prior to Diels-Alder reaction.[1]

FTMW spectroscopy is one of the most reliable methods to determine structural parameters accurately. In combination with a supersonic jet, this technique provides significant improvements in sensitivity and accuracy compared to absorption cells, enabling the measurements of isotopic species with even less than 1% natural abundance[2-4] to study the precise structure of a molecule and/or investigate its internal dynamics in form of various large amplitude motions (LAMs). Today, molecular jet FTMW spectroscopy is quite often combined with quantum chemical calculations, a helpful tool to predict the conformational landscape as well as geometry parameters such as rotational constants and LAM parameters e.g. the barrier hindering an internal rotation.

gauche 1,3-Butadiene is not the only case where the question “planar or not planar” raises contradicting answers. Systematic investigations on structures of alkyl ketones like ethyl methyl ketone[5] and diethyl ketone[6] have often indicated a discrepancy between the calculated structure and the experimentally determined one regarding the orientation of the alkyl chain. While quantum chemistry sometimes predicts that the alkyl group(s) should be tilted out of the C-(C=O)-C plane by a small angle, typically from 5° to 15°, a model for an effective planar molecule could be applied with success to reproduce the experimental spectra. Similar problems were encountered in investigations on aliphatic ketones with longer carbon chains such as pentan-2-one,[7] hexan-2-one[8] and heptan-2-one,[9] or even when the alkyl chain is branched as in the cases of pinacolone[10] and methyl neopentyl ketone.[11] A conclusive statement could not be drawn since the experimental data did not allow to confirm or deny a C_s structure, as no isotopic species could be measured.

In the present study, 2-propionylthiophene (2PT), a ketone where an ethyl group is attached on one side of the C=O bond and the planar thiophene ring on the other side (see Figure 1), was investigated by FTMW spectroscopy to gain experimental insight into the orientation of the propionyl moiety. It is known that if an ethyl group is attached to a frame with C_s symmetry, in the case of 2PT the (C_4H_3S)–C=O frame, it prefers two orientations: the C_s (or in-plane) conformer with the ethyl C–C bond also lying on the plane of the frame and the C_1 (*gauche* or out-of-plane) conformer with the methyl group tilted out of that plane.[12-16] For the carbonyl group, there are two possible

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Electronic Supplementary Information (ESI) available: Nuclear coordinates in the principal axis system of the conformers, calculated rotational constants and dihedral angles at different levels of theories, potential energy curve for the rotation of the methyl group of *syn*-2PT and frequency lists. See DOI: 10.1039/x0xx00000x

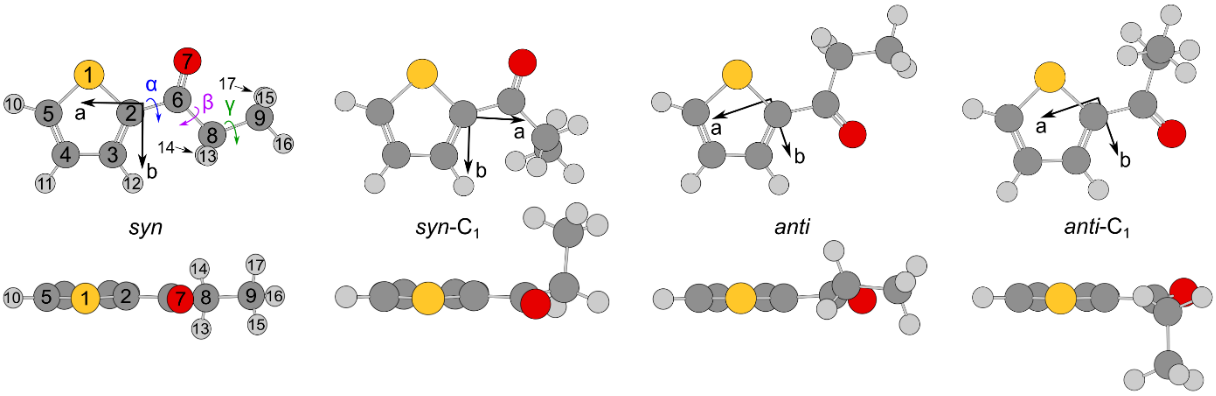

Figure 1. Molecular structures in front view (upper trace) and side view (lower trace) of four conformers of 2PT optimized at the MP2/6-311++G(d,p) level of theory their principal axes of inertia. The *syn*- and *anti*-conformers were observed in the experimental spectrum. Each of the conformers *syn*-C_1 and *anti*-C_1 exists as an image and a mirror image structure. Atom numbering and definitions of the dihedral angles are given at the *syn*-conformer.

are stabilized by π-conjugations.[17] Therefore, it was almost obvious to assume that four stable conformers of 2PT would exist with two possible orientations of the ethyl group (C_s and C_1) and two of the carbonyl group (*syn* and *anti*). We were interested in testing and validating this assumption, as well as in studying which conformers are present in the experimental spectrum. Regarding the planarity issue, we paid special attention to the *syn*- and *anti*-conformers (see Figure 1).

2 Quantum Chemical Calculations

Due to the known planarity of thiophene,[18,19] the conformational landscape of 2PT is entirely determined by the orientation of the propionyl moiety, expressed by the dihedral angles $\alpha = \angle(S1,C2,C6,O7)$ and $\beta = \angle(C2,C6,C8,C9)$. Varying α corresponds to a rotation of the thiophene ring about the C2–C6 bond, and varying β to the rotation of the ethyl group about the C6–C8 bond (for atom numbering see Figure 1).

Structure optimizations under full relaxation were carried out at the MP2/6-311++G(d,p) level of theory using the *Gaussian 16* programme package,[20] as this combination of method and basis set has yielded reliable starting values for the rotational constants of other molecules containing an ethyl group and an aromatic ring such as phenetole,[21] or an ethyl group and a carbonyl bond such as ethyl acetate,[22] methyl propionate,[23] and *N*,*N*-diethylpropionamide.[24] Potential energy scans performed by varying the dihedral angle α at a starting value of 180° for β yielded two stable conformers where the oxygen atom is either in a *syn*-orientation at α = 0° or in an *anti*-orientation at α = 180° relative to the sulphur atom of the thiophene ring. Full geometry optimizations revealed that the *syn*-conformer is energetically more favourable by 4.89 kJ/mol, whereby zero-point energy corrections have been taken into account. This is a result of the orbital interactions, mainly due to electrostatic interaction between the oxygen atom of the carbonyl group and the sulphur atom in the thiophene ring,[25] as has been reviewed and extensively discussed in Ref. 17.

Starting at either α = 0° or 180°, the dihedral angle β was subsequently varied in 10° steps, while all other geometry parameters including α were optimised. The potential energy points obtained from scans at α = 0° (*syn* conformations) were parameterized with a one-dimensional Fourier expansion. The potential curve was drawn using the obtained Fourier coefficients as illustrated in Figure 2. The Fourier coefficients are available in Table S1 in the Electronic Supplementary Information (ESI).

In total, four conformers were found on the potential energy surfaces, all of which were confirmed as true minima by frequency calculations. The so-called *syn*-conformer is energetically most stable with a *syn* orientation between the oxygen and the sulphur atoms and a nearly in-plane orientation of the propionyl chain. The entire propionyl group is tilted out of the thiophene plane by an angle of 2.6°, and the ethyl group is bent by 4.8° (see the values of α and β given in Table 1). In conformer *syn*-C_1 at $\beta \approx 80°$ and its energetically equivalent mirror image *syn*-C_1* at $\beta \approx -80°$, the methyl group is tilted out of the C-C=O-C plane by 78.7°. Two conformers with an *anti*-orientation between the two heteroatoms were also observed with similar positions of the ethyl group. The geometries of all conformers are illustrated in Figure 1; the atomic coordinates are given in Table S2 in the ESI. The optimizations were repeated using different combinations of methods and basis sets. The resulting rotational constants and dihedral angles α and β of the assigned conformers are given in Table S3. For the *syn*- and *anti*- conformers we found a notable difference in the optimized structures obtained at different levels of theory. Several MP2 levels predicted a small out-of-plane tilt angle for the propionyl and the ethyl groups with the dihedral angles α and β deviating by up to 8° from those of a planar structure, while all other methods yielded a perfect in-plane orientation of the entire propionyl group.

The energy difference between the conformers also depends on the method and basis set in use. An example is shown in Figure 2, where the difference between the *syn*- and *syn*-C_1-conformers is much higher in calculations with the

Table 1. Energy differences (in kJ/mol) including zero-point corrections between the four conformers of 2PT as well as the dihedral angles α and β (in degrees), rotational constants (in MHz) and dipole moments (in D).

	syn	***syn*-C₁**	***anti***	***anti*-C₁**
ΔE_{MP2}[a,b]	0.00	2.31	4.89	6.18
$\Delta E_{B3LYP\text{-}D3BJ}$[a,b]	0.00	2.28	2.71	4.82
$\Delta E_{M06\text{-}2X}$[a,b]	0.00	4.00	2.94	6.82
α_{MP2}[b]	−2.6	5.1	172.8	−170.8
β_{MP2}[b]	175.2	78.7	172.5	83.4
$\alpha_{B3LYP\text{-}D3BJ}$[b]	0.0	2.1	−180.0	−176.5
$\beta_{B3LYP\text{-}D3BJ}$[b]	−180.0	83.4	180.0	86.1
$\alpha_{M06\text{-}2X}$[b]	0.0	1.9	−180.0	−175.8
$\beta_{M06\text{-}2X}$[b]	180.0	79.9	−180.0	82.8
A_e[c]	3394.9	2617.5	3245.4	2547.6
B_e[c]	877.0	1029.0	904.8	1059.3
C_e[c]	703.1	800.9	716.0	826.0
A_0[d]	3394.0	2597.4	3235.0	2535.0
B_0[d]	866.0	1024.8	897.4	1055.4
C_0[d]	695.3	795.6	709.7	817.8
μ_a[e]	1.48	−1.07	−2.10	2.12
μ_b[e]	3.86	4.18	−2.34	−2.57
μ_c[e]	0.06	−0.09	−0.46	0.57

[a] Relative to the most stable conformer *syn*-2PT with E_{MP2} = −743.3985996 Hartree, $E_{B3LYP\text{-}D3BJ}$ = −745.1229209 Hartree and $E_{M06\text{-}2X}$ = −744.9051432 Hartree. [b] Calculated with the basis set 6-311++G(d,p). [c] Equilibrium rotational constants obtained from geometry optimizations at the MP2/6-311++G(d,p) level of theory. [d] Vibrational ground state rotational constants obtained from anharmonic frequency calculations at the MP2/6-311++G(d,p) level of theory. [e] Calculated at the MP2/6-311++G(d,p) level of theory.

B3LYP-D3BJ and M06-2X than those with the MP2 method. While all levels of theory consistently predict the *syn*-conformer to be lowest and the *anti*-C₁ to be highest in energy, the energy order between *syn*-C₁ and *anti*-2PT is method-dependent, as shown in Table 1. We have found similar disagreement in energy calculations at different levels of theory in some of our previous works.[24,26]

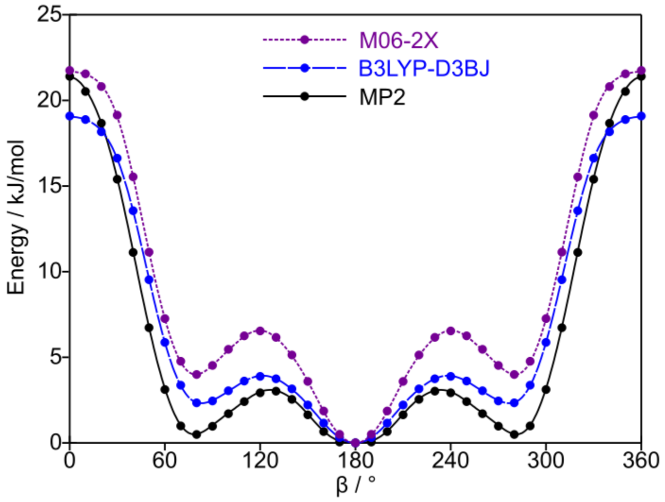

Figure 2. The relaxed potential energy scans of 2PT obtained by rotating the ethyl group about the C6–C8 bond in 10° steps calculated using the MP2, B3LYP-D3BJ and M06-2X methods in combination with the 6-311++G(d,p) basis set. All starting geometries possess a *syn*-orientation between the two heteroatoms of the molecule. The energies are given relative to the lowest energy conformation with E_{MP2} = −743.5311916 Hartree, $E_{B3LYP\text{-}D3BJ}$ = −745.1229207 Hartree and $E_{M06\text{-}2X}$ = −744.9051433 Hartree. The minimum at 180° corresponds to the *syn*-conformer and the minima at about ±80° to conformer *syn*-C₁ and its mirror image.

To determine the barrier to internal rotation of the methyl group, geometry optimisations were carried out by varying the dihedral angle γ = ∠(C6,C8,C9,H15) in steps of 10°. The threefold potentials of the most stable *syn*-conformer calculated at the MP2/6-311++G(d,p), B3LYP-D3BJ/6-311++G(d,p) and M06-2X/6-311++G(d,p) levels of theory are shown in Figure S1 in the ESI. The value of the barrier height predicted with different methods varies significantly, ranging from 764.5 to 929.3 cm^{-1} for the *syn*-conformer. Similar values are found for all other conformers. Therefore, torsional splittings in the microwave spectrum should be small, but resolvable with the resolution of our spectrometer.

3 Microwave Spectroscopy

3.1 Measurements

A broadband scan from 9.0 to 14.8 GHz as a series of overlapping spectra with a step width of 0.25 MHz was recorded using a molecular jet FTMW spectrometer operating in the frequency range from 2.0 to 26.5 GHz.[27] 2PT was purchased from TCI Europe, Zwijndrecht, Belgium, with a stated purity of 97 % and used without further purification. The substance was put on a pipe cleaner and placed upstream the nozzle with a backing pressure of 2 bar helium as the carrier gas. All signals appearing in the survey spectrum were later remeasured at higher resolution with an experimental accuracy of 2 kHz.[28] Figure 3 shows a part of the broadband scan from 9200 to 9500 MHz, where the arbitrary intensity is given in a logarithmic scale. The rotational temperature is estimated to be about 1-2 K.

3.2 Spectral assignment

We started the spectral assignment with the most stable *syn*-conformer. The equilibrium rotational constants A_e = 3394.9 MHz, B_e = 877.0 MHz and C_e = 703.1 MHz calculated at the MP2/6-311++G(d,p) level of theory were used to predict the rigid-rotor spectrum of *syn*-2PT. From the calculated dipole

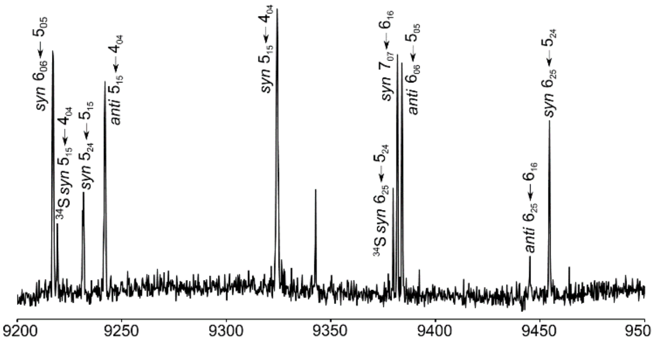

Figure 3. Broadband scan of 2PT in the frequency range from 9200 to 9500 MHz recorded by overlapping spectra with 50 co-added decays per each spectrum. The arbitrary intensity is given in a logarithmic scale. Each line is labelled by the rotational quantum numbers of the transition $J''_{K_a''K_c''} \leftarrow J'_{K_a'K_c'}$ and the corresponding conformer.

moment components of μ_a = 1.48 D, μ_b = 3.86 D and μ_c = 0.06 D, strong *b*-type, weaker *a*-type and no *c*-type transitions are expected in the spectrum. The assignment was straightforward, as the predicted rotational constants were sufficiently accurate.

After the spectrum of the *syn*-conformer was assigned, many lines with slightly lower intensity remained unassigned. The rigid rotor spectra of the *syn*-C_1-, *anti*- and *anti*-C_1-conformers were predicted and compared with the spectrum in which all lines belonging to *syn*-2PT had been excluded. Figure 4 clearly visualizes that almost all remaining lines belong to the *anti*-conformer. After the assignment of *anti*-2PT, only very few weak lines in the spectrum were unassigned, indicating that the *syn*-C_1 conformer is not present, although the calculated energies reported in Table 1 might suggest this. State-of-the-art computations reported in recent investigations in the literature have demonstrated well that not only the correct energy order, but also computed potential energy surfaces could explain the observation of only certain conformers as relaxation processes can be captured.[29,30] These can easily happen in non-covalent complexes as well as isolated molecules.[31]

In the high resolution spectra, small splittings from 2 to 50 kHz were observed for both conformers. They arise from the internal rotation of the methyl group and were primarily analysed for rotational transitions with high *J* and *K* quantum numbers. Figure 5 shows a high resolution measurement of the *b*-type $11_{1,10} \leftarrow 10_{2,9}$ transition which illustrates a typical splitting into an A and an E symmetry species. For several transitions, we found further smaller splittings, which might be caused by spin-spin or spin-rotation coupling of the hydrogen atoms, but most of the transitions only appeared broader. The average line width at half height (FWHM) is 20 kHz, although the variation between different transitions is significant. The estimated measurement accuracy, corresponding to 1/10 of the average line width, is 2 kHz.

In total, 150 A and 51 E symmetry species lines were assigned for the *syn*-conformer of 2PT, as well as 103 A- and 32 E-species lines for the *anti*-conformer. The much smaller number of E-species lines is due to the high rotational barrier, causing unresolved splittings in most of the transitions. As expected, only *a*- and *b*-type transitions were observed. The molecular parameters obtained from a fit using the program *XIAM*[32] are collected in Table 2. The assigned frequencies are listed in Table S5 and S6 in the ESI. The angles between the methyl rotor and the principal axes could not be fitted and were fixed to values calculated at the MP2/6-311++G(d,p) level of theory, which predicts a non-planar geometry for both *syn*- and *anti*-2PT, in agreement with the results from isotopic substitution (see section 3.4 and discussions which follow). The influence of the fixed values on the fit quality is, however, not significant. For comparison, the fits with the angles between the methyl rotor and the principal axes fixed to values calculated at the B3LYP-D3BJ/6-level, which predicts a planar geometry for both conformers, are given in Table S7. Because only transitions in the torsional ground state are available, the rotational constant F_0 of the methyl group could not be fitted and was fixed to 160 GHz, a value often found for methyl rotors.

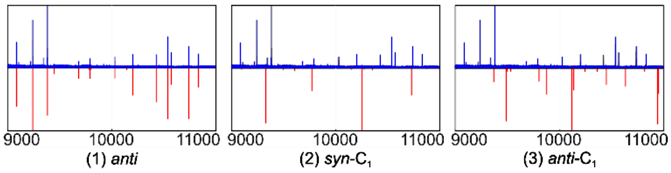

Figure 4. The upper trace of all sub-figures illustrates the experimental broadband scan from 9000 to 11000 MHz where all lines belonging to *syn*-2PT have been excluded. The lower trace of figure (1) shows the fitted spectrum of *anti*-2PT and that of figures (2) and (3) the theoretical spectrum of *syn*-C_1-2PT and *anti*-C_1-2PT, respectively, calculated from their equilibrium rotational constants. The present figure indicates that beside *syn*-2PT only the *anti*-conformer is present in the experimental spectrum.

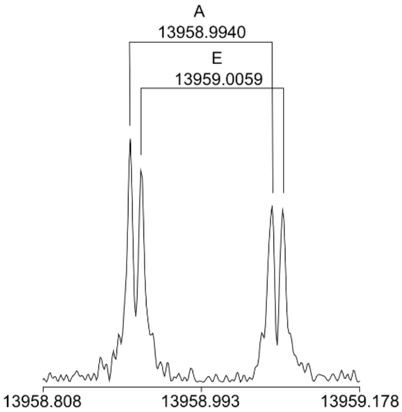

Figure 5. A high resolution spectrum of the *b*-type transition $11_{1,10} \leftarrow 10_{2,9}$ of *syn*-2PT. The splittings indicated by brackets are due to the Doppler effect; the frequencies are given in MHz. The polarization frequency is 13958.98 MHz. The A and E symmetry species are found at 13958.9940 MHz and 13959.0059 MHz, respectively, corresponding to a torsional splitting of 11.9 kHz. For this spectrum, 1168 free induction decays were co-added.

Table 2. Molecular parameters of the *syn*- and *anti*-conformers of 2PT obtained with the program *XIAM*.

Par.[a]	**Unit**	***syn***	**Calc.**[b]	***anti***	**Calc.**[b]
A_0	MHz	3427.43880(19)	3393.970	3274.03476(39)	3234.681
B_0	MHz	877.177065(48)	865.960	905.747009(78)	897.435
C_0	MHz	704.893298(31)	695.289	716.231432(37)	709.719
D_J	kHz	0.01812(15)	0.0178	0.02330(31)	0.0237
D_{JK}	kHz	0.0749(27)	0.0718	0.0621(69)	0.0313
D_K	kHz	0.4473(93)	0.4816	1.842(58)	0.5442
d_1	kHz	−0.00370(10)	−0.0039	−0.00639(30)	−0.0059
d_2	kHz	−0.000275(69)	−0.0004	−0.00138(25)	−0.0092
V_3	cm^{-1}	806.94(54)	929.3	864.5(88)	919.9
∠(*i*,*a*)	deg	19.9[c]	19.9	11.2[c]	11.2
∠(*i*,*b*)	deg	70.4[c]	70.4	80.9[c]	80.9
∠(*i*,*c*)	deg	86.9[c]	86.9	83.4[c]	83.4
N_A/N_E[d]	-	150/51		103/32	
σ[e]	kHz	2.6		2.5	

[a] All parameters refer to the principal axis system. Watson's S reduction and I^r representation were used. [b] Ground state rotational constants and centrifugal distortion constants from anharmonic frequency calculations, all other parameters from optimisations at the MP2/6-311++G(d,p) level of theory. [c] Fixed to the values calculated at the MP2/6-311++G(d,p) level, predicting a non-planar geometry, in agreement with the results from isotopic substitutions. [d] Number of A and E species transitions. [e] Standard deviation of the fit.

3.3 Isotopologues

As mentioned in Section 2, quantum chemical calculations predicted the propionyl group of the *syn*- and *anti*-conformers to be either perfectly in-plane or slightly tilted out of the thiophene frame, depending on the level of theory in use. To investigate this issue experimentally, we searched for the spectra of the ^{34}S and three ^{13}C-isotopologues C(6), C(8) and C(9) in natural abundances of 4.25% and 1.07%, respectively.[33] The Cartesian coordinates of the optimized structure given in Figure 1 were taken, and the mass of the individual carbon atoms and the sulphur atom was adjusted to calculate the rotational constants of the isotopologues. The predicted ^{34}S- and ^{13}C-frequencies ν_{calc}^{iso} were corrected with the differences $\Delta\nu_{cal}$ between the frequencies predicted with the B_e rotational constants obtained at the MP2/6-311++G(d,p) level ν_{calc}^{parent} and the experimental frequencies ν_{obs}^{parent} of the main species, leading to successful assignments of all four isotopologues using the corrected frequencies ν_{iso}.

$$\Delta\nu_{cal} = \nu_{obs}^{parent} - \nu_{calc}^{parent} \tag{1}$$

$$\nu_{iso} = \nu_{calc}^{iso} + \Delta\nu_{cal} \tag{2}$$

Only the ^{13}C isotopologues at the positions relevant to determine the orientation of the propionyl moiety were investigated. The search was time-consuming since ^{13}C signals of 2PT were quite weak and often underlay the much more intense ^{12}C signals. The C(2) atom lies very close to the centre of mass of the molecule. Therefore, the spectrum of its ^{13}C-isotopologue could not be captured because all signals are at nearly the same frequencies as those of the main isotopologue. Assuming that the thiophene ring is planar as expected for an aromatic system, the ^{34}S-isotopologue was chosen to substitute ^{13}C(2). The molecular parameters of four isotopologues of *syn*-2PT are collected in Table 3. The lists of fitted transitions and their residuals are available in Tables S8 of the ESI. No internal rotation splittings were found for all measured isotopologue transitions.

Only the ^{34}S-isotopologue of *anti*-2PT could be tentatively assigned and the number of lines is very small (see also Table S8). For the three *anti*-2PT ^{13}C-isotopologues, there are not enough observable transitions to support a convincing assignment, as the transitions were too weak or covered by the much stronger ^{12}C signals or the cavity resonance.

Table 3. Rotational constants (in MHz) and centrifugal distortion constant D_J (in kHz) of four isotopologues of *syn*-2PT obtained with the program *XIAM*.

Par.[a]	**^{34}S**	**^{13}C(6)**	**^{13}C(8)**	**^{13}C(9)**
A_0	3376.65668(41)	3426.27459(41)	3409.99595(54)	3424.61165(29)
B_0	870.92399(28)	875.10430(27)	869.790462(27)	857.46947(20)
C_0	698.70339(37)	703.50933(12)	699.391506(15)	691.999904(95)
D_J	0.0217(52)	0.01812[b]	0.01812[b]	0.01812[b]
N[c]	23	15	14	12
σ[d]	3.9	2.5	3.0	1.6

[a] All parameters refer to the principal axis system. Watson's S reduction and I^r representation were used. [b] Values of all centrifugal distortion constants except D_J of the ^{34}S species could not be fitted and are fixed to those of the main isotopologue given in Table 2. [c] Number of lines. [d] Standard deviation of the fit in kHz.

3.3 Structure determination

The partial r_s structure of *syn*-2PT was derived from multiple isotopic data using the rotational constants of the parent species given in Table 2 and those obtained for the four isotopologues collected in Table 3. The position of each substituted atom was first calculated using Kraitchman's equations[34] implemented in the program KRA available from the PROSPE website,[35] which provides the absolute atomic coordinates in the principal axis system. The uncertainties were calculated according to Costain's rule.[36] The signs of the atom coordinates were taken to be consistent with the optimized geometry. The resulting atomic coordinates are given in Table 4. The bond lengths, bond angles, and the desired dihedral angle θ = ∠(S1,C6,C8,C9) were determined with the program EVAL, also available at the PROSPE website,[35] and are given in Table 5. These geometry parameters are compared with those of the equilibrium structure r_e obtained from geometry optimizations with the MP2, B3LYP-D3BJ and M06-2X methods. We note that the predicted values refer to the equilibrium configuration of the molecule, while vibrational effects affect the substitution geometry. This limits the accuracy of the obtained r_s structural parameters. A better alternative would be the semi-experimental equilibrium structure[37,38] which is unfortunately not possible due to the limited number of assigned isotopologues for *syn*-2PT.

4 Discussion

4.1 Conformational stability

Four stable conformers of 2PT were predicted by quantum chemistry. Regarding the orientation of the carbonyl group, a *syn*- and an *anti*-form are stable. Their stability arises from interactions between the aromatic ring and the carbonyl group, as well as conjugation effects which favour planar forms due to a maximum overlap between the π-orbitals. The higher stability of the *syn*-form of 2PT is mainly due to electrostatic interaction between the oxygen atom of the carbonyl group and the sulphur atom in the ring.[25] The opposite charges on the oxygen and sulphur atoms stabilise the *syn*-conformers, as visualised in Figure 6 with the charge data obtained from NBO calculations. For each of the *anti*- and *syn*-forms, two further conformers are stable. They differ by the orientation of the ethyl group (nearly in-plane or out-of-plane C_1), resulting in a total of four conformers for 2PT. The stability between the forms varies in different molecules. The energetically most favourable conformer predicted by all levels of theory in use, *syn*-2PT, has a *syn*-orientation between the oxygen and sulphur atoms and an in-plane or "nearly in-plane" propionyl group. This is in agreement with the intensity observed in the spectrum under our measurement conditions, where the most intense signals signals belong to *syn*-2PT. The *anti*-C_1 conformer is predicted to be highest in energy, which is confirmed by the experiment as it was not observed in the microwave spectrum. The stability of

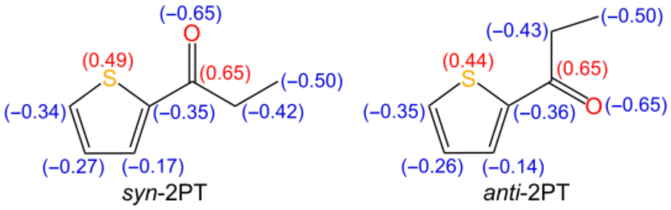

Figure 6. Charge distribution in *syn*- and *anti*-2PT obtained from NBO calculations at the MP2/6-311++G(d,p) level of theory.

syn-C_1- and *anti*-2PT is controversial, because some levels predict that *syn*-C_1 is more stable, while *anti*-2PT is more stable in calculations at other levels. The latter matches the result from experiments, as beside *syn*-2PT, only *anti*-2PT was assigned. The spectrum of *anti*-2PT is slightly weaker than that of *syn*-2PT, but also quite intense, as illustrated in Figure 3. From the values of the dipole moment components given in Table 1, *a*-type transitions of *anti*-2PT are expected to be higher in intensity than those of *syn*-2PT. However, experimentally both *a*- and *b*-type transitions of the *syn*-conformer are always stronger, further confirming the energetical favourability of this conformer. The *a*- and *b*-dipole moment components of the two non-assigned C_1 conformers are very similar to the corresponding assigned ones. Therefore, low dipole moments are not the reason for their non-visibility in the spectrum. Obviously, a planar orientation of the ethyl group has a more significant impact on the conformational stability over electrostatic effects which would favour *syn*-C_1-2PT over *anti*-2PT.

4.2 Quality of the fit

In total, 201 and 135 lines of the *syn*- and *anti*-conformers, respectively, of 2PT were assigned and fitted with the program *XIAM*. The standard deviation of the *syn*-2PT fit is 2.6 kHz; that of *anti*-2PT 2.5 kHz; both are in good agreement with the experimental accuracy of about 2 kHz. The fit quality is therefore satisfactory. All rotational and centrifugal distortion constants are determined with high accuracy. The angles between the internal rotor axis and the principal axes cannot be determined well and thus have been fixed to the values determined from geometry optimisations at the MP2/6-311++G(d,p) level of theory, as this level predicted a tilt angle of the ethyl group, in agreement with the results from structure determinations given in Section 3.4.

4.3 Molecular geometry

The experimentally deduced rotational constants are in good agreement with the B_e constants predicted at the MP2/6-311++G(d,p) level of theory, which has eased the assignment process significantly. The basis set variation (see Table S3 in the ESI) shows, that the predicted rotational constants agree within 1% with the experimental values for most method-basis set combinations. The error compensations at the B3LYP-D3BJ/cc-pVTZ level of theory yield B_e constants which are in exact agreement with the experimental values of both conformers, followed by those of the Truhlar's M06-2X/cc-pVDZ level. Though it is not physically meaningful to compare predicted B_e

Table 4. Experimental atom positions of the partial substitution r_s structure of *syn*-2PT obtained by isotopic substitutions with Kraitchman's equations[34] as implemented in the program KRA,[35] For comparison, atom positions of the equilibrium r_e structures optimized at the MP2/6-311++G(d,p), B3LYP-D3BJ/6-311++G(d,p) and M06-2X/6-311++G(d,p) levels of theory are also given. Standard errors in parentheses are in the unit of the least significant digits.

	r_s			r_e^{MP2}		
	|*a*| / Å	**|*b*| / Å**	**|*c*| / Å**	***a* / Å**	***b* / Å**	***c* / Å**
S1	1.4459(10)	1.0663(14)	0.025(58)	1.456117	−1.068910	−0.001120
C6	1.1694(13)	0.2197(68)	0.046(32)	−1.185448	−0.244282	0.007579
C8	2.21342(68)	0.8730(17)	0.060(25)	−2.210229	0.878001	0.051818
C9	3.64496(41)	0.3512(43)	0.050(29)	−3.643985	0.365936	−0.032649
	r_e^{B3LYP}			$r_e^{M06\text{-}2X}$		
	***a* / Å**	***b* / Å**	***c* / Å**	***a* / Å**	***b* / Å**	***c* / Å**
S1	1.465167	−1.075649	0.000070	1.458905	−1.069740	−0.000049
C6	−1.184143	−0.241682	−0.000106	−1.186286	−0.241721	0.000022
C8	−2.222044	0.872099	−0.000075	−2.212429	0.876447	0.000077
C9	−3.656592	0.354577	0.000247	−3.640857	0.351739	0.000033

Table 5. Bond lengths (in Å), bond angles and the ∠(S1,C6,C8,C9) dihedral angle (in degrees) of *syn*-2PT deduced from the atom coordinates given in Table 4. The signs of the r_s atom coordinates used to determine these parameters were taken to be consistent with the optimized geometry as indicated in the superscript.

	r_s^{MP2}	r_e^{MP2}	$r_s^{B3LYP\text{-}D3BJ}$	$r_e^{B3LYP\text{-}D3BJ}$	$r_s^{M06\text{-}2X}$	$r_e^{M06\text{-}2X}$
C6–C8	1.5113(52)	1.5204	1.5113(52)	1.5224	1.5113(52)	1.5177
C8–C9	1.5277(33)	1.5248	1.5277(33)	1.5250	1.5237(18)	1.5218
S1–C6–C8	151.62(33)	149.71	151.62(33)	150.45	151.62(33)	149.92
C6–C8–C9	113.56(31)	112.60	113.56(30)	113.14	113.66(26)	112.37
S1–C6–C8–C9	**173.0(42)**	**178.36**	**−173.0(42)**	**−179.98**	**177.1(42)**	**180.00**

constants with experimental B_0 constants, the B3LYP-D3BJ/cc-pVTZ and M06-2X/cc-pVDZ levels offer cost-efficient calculations with accidentally good accuracy to be useful in guiding the assignment of vibrational ground state microwave spectra. Therefore, they are recommended for molecules related to 2PT.

The distance of the C(6)–C(8) and the C(8)–C(9) bonds of 1.5113(52) and 1.5277(33) Å are typical values for a C–C single bond in an ethyl moiety, as found in previous investigations where experimental bond lengths are reported for the ethyl group.[26] The dihedral angle $\theta = \angle(\mathrm{S1,C6,C8,C9}) = 173.0(42)°$ deduced from the partial r_s structure confirms a non-planar heavy atom skeleton of the most stable *syn*-conformer, which is predicted at some MP2 levels of theory. Because the signs of the coordinates cannot be determined from Kraitchman's equations, the quantum chemistry level chosen for the signs of the coordinates slightly affects the obtained structural properties. This especially influences the *c*-coordinates since their signs are level-dependent. It is not surprising, because the values of the *c*-coordinates are close to zero, which is also the reason why they are determined with much less accuracy than those of the *a*- and *b*-coordinates (see Table 4). The dihedral angle θ is affected most significantly by the sign choice for the *c*-coordinates and varies between 173.0(42)° and 177.1(42)° (see Table 4). Though there is only a thin border between "planar" and "not planar" because the tilt angle, if it exists, is quite small, a comparison with the predicted θ values of either 180° in the case of a planar structure or about 178° for a non-planar structure shows, that the experimental structure of 2PT is *not* planar. The experimentally determined *c*-coordinates given in Table 4 also confirm this conclusion.

The inertial defects $\Delta_c = I_c - I_a - I_b$ of the *syn*- and *anti*-conformers are –6.635 uÅ² and –6.720 uÅ², respectively. The Δ_c values of "perfect C_s" molecules containing an ethyl group, for example the *cis-trans* conformer of ethylnitrite (Δ_c = –6.422 uÅ²)[39] and the C_s conformer of 2-ethylfuran (–6.483 uÅ²)[26] indicate the contribution of four out-of-plane hydrogen atoms on this parameter. The value of –6.635 uÅ² for *syn*-2PT and –6.720 uÅ² for the *anti*-conformer is higher than those of *cis-trans*-ethylnitrite and C_s-2-ethylfuran, further supporting a non-planar structure of *syn*-2PT and *anti*-2PT with a slight tilt angle of the ethyl group. For comparison, a non-planar structure where the methyl group in the ethyl moiety is completely out of the (C=O)-C plane would lead to a significantly higher value of the inertial defect, as in the case of the C_1 conformer of 2-ethylfuran (–29.851 uÅ²).[26]

4.4 Barrier to methyl internal rotation

Barriers to internal rotation of ethyl methyl groups are usually higher than 1000 cm⁻¹, which often inhibit the torsional splittings to be resolved. Therefore, in many investigations, no information on the methyl torsion was reported, though the molecules contain one or more methyl groups, e.g. in Ref. 40-45. In some when the barrier heights could be determined, values of over 1000 cm⁻¹ have often been found.[46,47] For 2PT, the barrier to internal rotation of 806.94(54) cm⁻¹ for the *syn*-conformer and 864.5(88) cm⁻¹ for the *anti*-conformer is significantly lower. This can be explained by the presence of the carbonyl group to which the ethyl group is attached, similar to the cases of ethyl methyl ketone (763.87(65) cm⁻¹),[5] diethyl ketone (771.93(27) cm⁻¹),[6] methyl propionate (820.46(99) cm⁻¹),[23] propionic acid (818(11) cm⁻¹)[48] and propionyl fluoride (839(21) cm⁻¹).[49] Though the number of investigated molecules containing a propionyl group (an ethyl group attached to a carbonyl bond) is rather small, there are enough data points to support the conclusion that the torsional barrier of the methyl group in the propionyl moiety is always around 800 cm⁻¹. It is interesting to note that in the case of α-fluoropropionic acid, where a fluorine atom is attached at the α-carbon of the ethyl group, Eijck and Zoeren found a torsional barrier of 1129(42) cm⁻¹,[50] showing that an α-substitution in the propionyl group would bring the barrier height back to a value of over 1000 cm⁻¹.

5. Conclusion

Quantum chemical calculations predict four stable conformers for 2PT with different orientations of the propionyl group. The microwave spectra of two conformers, *syn*- and *anti*-2PT, were assigned under molecular jet conditions. The very small splittings due to internal rotation could be resolved for both conformers. Analysing the splittings with the program *XIAM* yielded torsional barriers of 806.94(54) cm⁻¹ for the *syn*- and 864.5(88) cm⁻¹ for the *anti*-conformer. Though the *syn*-configuration is favoured by electrostatic interactions of the opposite charges of the oxygen and sulphur atoms, the conformational stability of 2PT is decided by the orientation of the ethyl group. The planarity of 2PT is a controversial issue for calculations at different levels of theory, regarding whether the propionyl group is in-plane with the thiophene ring or not. Partial r_s structure determination from isotopic substitution of the most stable *syn*-conformer convincingly confirmed that 2PT is not planar. There is a tiny, but non-zero tilt angle between the ethyl group and the thiophene ring.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

We thank Hajar Bouzouma for her contribution within a student research project. Simulations were performed with computing resources granted by the RWTH Aachen University under the projects rwth0369 and rwth0506. This work was supported by the Agence Nationale de la Recherche ANR (project ID ANR-18-CE29-0011).

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