

Extensive study of the electron donor 1,1,4,4-tetrathiabutadiene (TTB) and of its charge transfer crystal with TCNQ

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ABSTRACT

In the spirit of the renewed interest in mixed stack charge-transfer (CT) crystals, made up by alternating π electron-donor and acceptor molecules, we focus attention on a forgotten donor, 1,1,4,4-tetrathiabutadiene (TTB), synthesized more than 35 years ago. We present a spectroscopic and computational characterization of the neutral TTB, and fully characterize the CT crystal with TCNQ. TTB-TCNQ is a mixed stack crystal, with limited degree of CT (about 0.1), despite TTB electron donating strength is only a little smaller than that of the famous TTF. This finding is explained by the small value of the Madelung energy, that we evaluate by a well tested computational approach.

Keywords:

π -electron donor
Mixed stack charge transfer
crystals Organic semiconductors
DFT

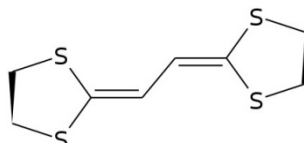
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1. Introduction

Interest in mixed stack organic charge transfer (CT) crystal has been recently renovated by their potential application as ambipolar semiconductors [1] or as ferroelectrics [2]. In this context, there has been a flourishing of papers aimed at characterizing different combinations of electron donor (D) and acceptor (A) molecules [3–8], in order to acquire knowledge on the structure-properties relations, and eventually gain control on the packing design, the band gap, and the degree of charge transfer (ρ) of these systems. Besides synthesizing new D and A molecules, there has been a rediscover of old systems, e.g., DBTTF-TCNQ [9,10], investigated through modern methods. Following the latter approach, we found an interesting electron donor, 1,1,4,4-tetrathiabutadiene (TTB, Scheme 1), for which just the

synthesis and a preliminary characterization of its CT crystals is present in the literature [11]. Here we report a detailed spectroscopic, structural and computational characterization of TTB and of the corresponding co-crystal TTB-TCNQ, extending the knowledge basis of mixed stack CT crystals, and showing that this forgotten molecule and its variants have the potential of affording new systems with perspective applications.



Scheme 1: TTB

2. Experimental Methods

Sample preparation

The donor TTB was synthesized following the procedure sketched in Ref. [11], that is by coupling of ethanedithiol and dimethoxydihydrofuran in the presence of BF_3 and subsequent oxidation of the resulting compound. Complete synthetic procedure and characterization is reported in the Supporting Information. Crystals of TTB-TCNQ several mm long were obtained by the slow diffusion at room temperature of two saturated acetonitrile solutions of the components. Millimeter size crystals could be extracted after five days.

X-ray diffraction measurements

A single crystal of TTB-TCNQ was mounted on a Bruker SMART 1000 CCD diffractometer equipped with graphite monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) fine-focus sealed tube. The intensity data were collected using ω scan at 295(2) K. Cell refinements and data reductions were performed using the Bruker SAINT software [12]. The structures were solved by direct methods using the program SIR97 [13] and refined with full-matrix least-squares based on F^2 using the program SHELXL2014/7 [14]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed geometrically and refined using a riding model approximation, with $\text{C-H} = 0.93\text{-}0.97 \text{ \AA}$ and with $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{C})$. The molecular graphics were prepared using Mercury [15] and Jmol [16] programs.

Spectroscopic measurements

Infrared (IR) spectra of the crystals were recorded with a Bruker IFS66 Fourier transform IR (FT-IR) spectrometer coupled to an IR microscope Hyperion 1000. Spectral resolution: 2 cm^{-1} . The Raman spectra were recorded with a Renishaw 1000 Raman spectrometer equipped with the appropriate edge filter, and coupled to a Leica M microscope. A Lexel Kr laser was used as light source. Exciting line: 676 nm.

3. Computational Methods

The vibrational frequencies of TTB and TTB^+ have been calculated with the GAMESS package [17], using Density Functional (DFT) with unrestricted B3LYP and the 6-31G(d) basis set. This combination is known to satisfactorily reproduce the molecular vibrations of relatively large organic molecules, provided tight geometry optimization and fine grids are used in the DFT analysis [18]. To calculate the CT integral of TTB-TCNQ we have followed the dimer approach [19,20], using the Gaussian09 package [21] to compute singlet and triplet ground states for a DA dimer. The basis set was again 6-31G(d), whereas we chose the unrestricted ω B97XD functional, which is more suitable for modeling intermolecular CT. The average charge residing on TTB and TCNQ molecules has been estimated on the basis of the computed Hirshfeld atomic charges [21]. The electrostatic interaction V within a DA pair and the Madelung energy M have been calculated by adopting the point-charge approximation of the molecular charge density based on ESP atomic charges. The crystal electrostatic sums have been obtained for finite clusters of increasing size using the MESCAL code [22].

4. Results and Discussion

4.1 TTB

The minimum energy conformation of neutral and ionic TTB in gas phase has C_i symmetry, with a planar central skeleton and out-of-plane staggered arrangement of the terminal $\text{CH}_2\text{-CH}_2$ groups. As chemical intuition suggest, the HOMO is concentrated on the double bonds and sulfur atoms (Figure 1). The former will then be weakened upon electron removal, as it happens with electron Donors based on the tetrathiafulvalene (TTF) skeleton.

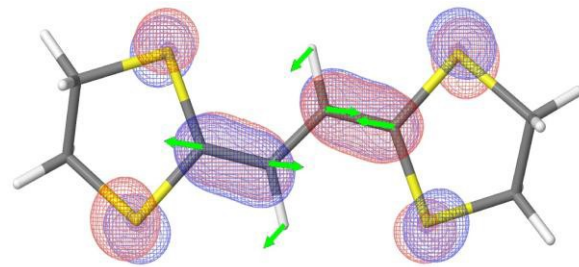


Fig. 1. Representation of the TTB HOMO. The eigenvectors of the IR active antisymmetric C=C stretching vibration are also shown (green arrows).

The HOMO energy can be taken as a relative measure of the ionization potential. The TTB HOMO energy is calculated to be - 4.59 eV, only 0.13 eV lower than that of TTF (- 4.46 eV, calculated by the same method). Then apparently the electron donor strength of TTB is only slightly smaller than that of TTF, in agreement with measured UPS vertical-ionization energy, less with the relevant ionization potentials [11].

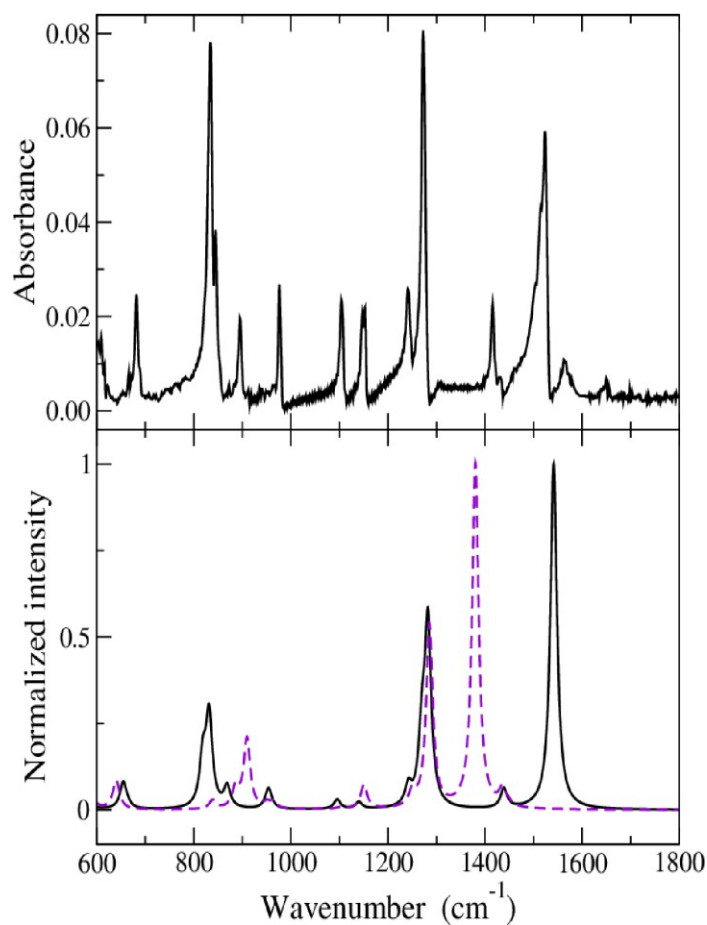


Fig. 2. Top panel: Experimental IR spectrum of TTB powders. Bottom panel: Calculated IR spectrum of neutral TTB (black line) and TTB⁺ (violet dashed line).

For the free TTB molecule in the C_i conformation, group theory predicts 30 vibrational modes of a_g symmetry, active in Raman, and 30 modes of a_u symmetry, infrared (IR) active. Calculations yield the vibrational assignment of the neutral molecule, as reported in the Supporting Information. The experimental IR and computed spectra are compared in Fig. 2. The calculated IR spectrum of TTB⁺ is also reported in the same Figure, in order to put in evidence the charge sensitive vibrational modes which allow the estimation of the degree of charge transfer [23,24] in the CT complexes in which TTB may be involved. It is seen that the antisymmetric C=C stretching, whose eigenvectors are pictorially represented in Fig. 1, and occurring at 1524 cm⁻¹, is the one exhibiting the largest ionization frequency shift, about 160 cm⁻¹. Of course, also the corresponding Raman active C=C symmetric stretching (Table S1) has a large ionization shift, but this mode mixes with the symmetric stretching of the central C-C bond, and in any case the totally symmetric modes, being coupled with the CT electron, cannot be used to estimate the ionicity of mixed stack CT crystals [25]. We finally notice that the a_u C-S stretching mode located at 834 cm⁻¹ is expected to exhibit a considerable (about 70 cm⁻¹) *upward* frequency shift upon ionization (Fig. 2 and Table S1).

4.2 TTB-TCNQ

TTB-TCNQ crystallizes in the triclinic system, space group P-1, with one DA pair per unit cell. The basic crystallographic parameters are reported in Table 1. Full information is given in the deposited CIF files (CCDC: 1576020). The present structure is different from the monoclinic one reported in Ref. [11], probably a case of polymorphism due to a different crystallization procedure.

Table 1. Room temperature crystal structure of TTB-TCNQ

Space group	<i>P</i> -1
<i>Z</i>	1
<i>T</i> / K	294(2)
<i>a</i> /Å	6.9177(7)
<i>b</i> /Å	8.9769(9)
<i>c</i> /Å	9.0882(9)
α (deg)	68.2461(15)
β (deg)	77.9771(17)
γ (deg)	88.7500(18)
<i>V</i> /Å ³	511.728
R, wR2 factor	4.26, 0.109

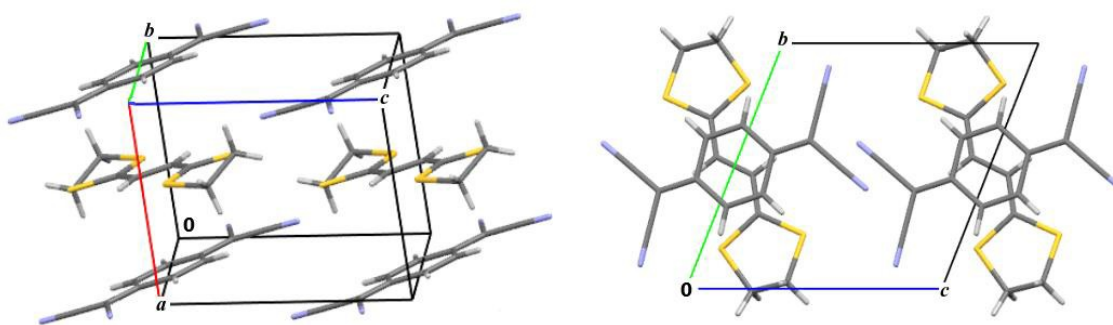


Fig. 3. Left panel: Crystal structure of TTB-TCNQ. Right panel: Crystal structure of TTB-TCNQ viewed from the a stack axis

Fig. 3 reports two views of TTB-TCNQ crystal structure. The left view shows the ..DADA ... stacking along the a crystal axis, and the right view puts in evidence the TTB – TCNQ overlay, with the long axes of the two molecules approximately perpendicular one another, in such a way to maximize the frontier orbital overlap.

TCNQ bond distances have been often used to estimate the degree of charge transfer ρ . If we follow the calibration of Ref. [5], we find a practically zero value. A generally more trusted procedure for estimating ρ is based on the frequency shift of some vibrational modes that are sensitive to the molecular charge [23,24]. For mixed stack CT crystal, one has to rely on the IR spectra, as the Raman active a_g vibrations are affected by the interaction with the CT electron [25].

Fig. 4 reports the polarized IR spectra of TTB-TCNQ in the spectral regions of the charge sensitive vibrations. The rightmost panel shows the frequency range of the CT transition, and will be discussed separately. The continuous black line in the Figure represents the absorption spectrum polarized perpendicularly to the stack, where the in-plane charge sensitive vibrations occur. Red and green dashed lines on top of the spectra indicate the frequency of the charge sensitive vibrations in neutral TCNQ and TTB, respectively, showing at a glance that TTB-TCNQ is well on the neutral side. The assessment of the actual ρ value is however difficult in the present case. In fact, the CN stretching

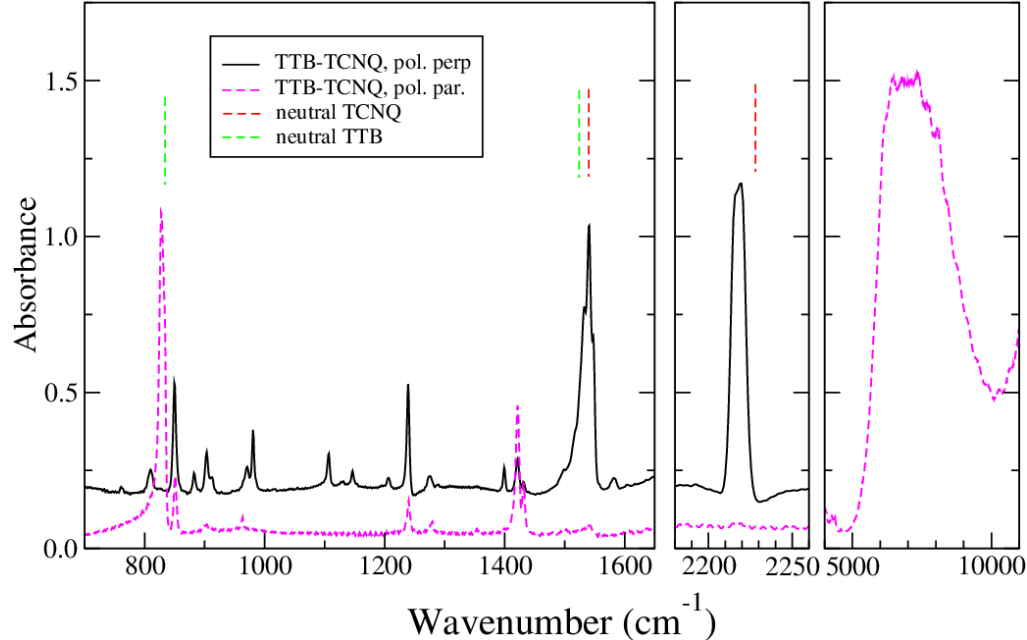


Fig. 4. Polarized IR spectra of TTB-TCNQ in the spectral regions of the charge sensitive vibrations and of the CT transition. Black continuous line: electric vector perpendicular to the stack axis. Magenta dashed line: electric vector parallel to the stack axis. The spectra are offset for clarity. Red and green dashed lines indicate the frequency of the charge sensitive vibrations in neutral TCNQ and TTB, respectively.

frequency, occurring at 2218 cm^{-1} , indicates $\rho = 0.2$, but the CN stretching frequency is known to give unreliable, generally overestimated, ρ values [26]. On the other hand, the TCNQ $b_{1u}v_{20}$ C=C antisymmetric stretching is very close to the analogous vibration of TTB $a_u v_{36}$: In neutral TCNQ and TTB they occur at 1545 [27] and at 1524 cm^{-1} (Table S1), respectively. In this spectral region TTB-TCNQ exhibits an absorption with a complex structure, with several peaks. If we attribute the main peak, at 1540 cm^{-1} , to the TCNQ vibration, we find $\rho = 0.1$, but the frequency of the TTB mode is not safely identified. Finally, the C-S antisymmetric stretch of TTB is located at 850 cm^{-1} , slightly upward in respect to the neutral molecule, as expected, but its precise calibration and actual ionization frequency shift are presently not known. The Raman spectra, shown in Fig. 5, confirms that TTB-TCNQ is well on the neutral side, as the observed frequencies are very close to the ones of the neutral molecules – the effect of the interaction of the totally symmetric modes with the CT transition is small when ρ is close to 0 or 1 [25]. To summarize, from vibrational spectra we estimate the degree of CT of TTB-TCBQ around 0.1, with a rather large uncertainty (± 0.06).

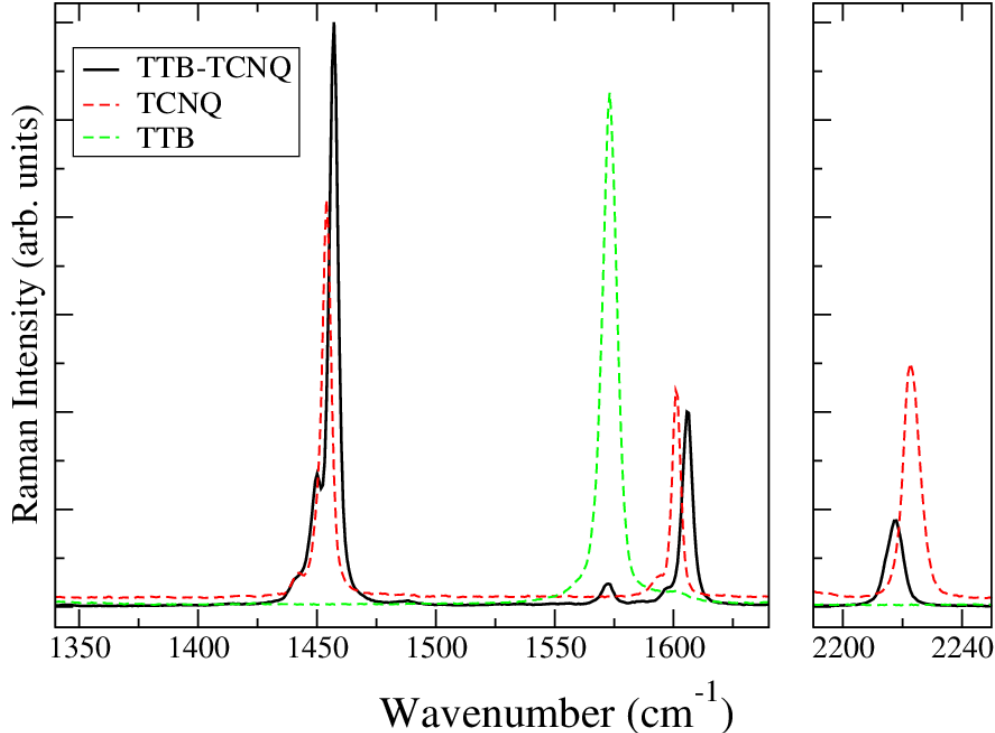


Fig. 5. Raman spectrum of TTB-TCNQ (black line) in the spectral region of the frequency sensitive modes. The Raman spectra of neutral TCNQ (dashed red line) and of TTB (dashed green line) are also shown for comparison. Exciting line: 676 nm.

The absorption spectrum in the leftmost panel of Fig. 4, with polarization along the stack axis, locates the CT transition of TTB-TCNQ. We explicitly remark that we had problems in recording this part of the spectrum, since the samples are relatively thick, of prismatic shape, and quite often geminated. We attempted to obtain reflectance spectra, but the reflectivity is low and distorted by multiple internal reflections. The absorption spectrum of Fig. 4 clearly saturates in this spectral region, and the absorbance cannot be compared with that of the other two panels in the Figure. Nevertheless, the spectrum allows to estimate the frequency of the CT transition at about 7000 cm^{-1} , or 0.87 eV . From the frequency of the CT transition, the above guess of ρ , and the model calculation of Ref. [28], we can estimate the value of the DA hopping or CT integral, t , as 0.16 eV .

Some of us have recently developed a method to estimate relevant model parameters of mixed stack CT crystals via density-functional theory calculations [20]. Briefly, one calculates the singlet and triplet

lowest energy states for an isolated DA pair by keeping the geometry fixed at the one found from the X-ray analysis of the crystal. From these results one can evaluate t and z , half the energy required to form an ionic pair. Furthermore, from the calculation of the charge distribution of both D and A in the neutral and fully ionized state, one calculates V , the DA intermolecular Coulomb potential, and M , the Madelung energy. In the present case, we find $t = 0.21 \text{ eV}$, in satisfactory agreement with the above

experimental estimate, and $z = 0.48$ eV. Moreover, $V = -1.92$ eV and $M = -0.97$ eV. If we compare these values with those obtained for the 11 mixed stack CT crystals considered in Ref. [20], we see that t is on the lower side of the spanned values, and z reflects the TTB ionization potential. The Madelung energy, on the other hand, is among the smallest in the series, a fact that explains why TTB-TCNQ charge transfer in the crystal is well on the neutral side.

5. Conclusions

In summary, we have characterized an old, little studied electron donor and its mixed stack CT crystal with TCNQ. Whereas its ionization potential is not dramatically higher than that of TTF, the degree of CT in TTB-TCNQ is low. We think that this fact is due to the molecular arrangement of the molecules within the crystal, which is a compromise between the overlap between the frontier orbitals of the two molecules and the steric hindrance. TTB and TCNQ long axes are almost perpendicular one another, and this makes the 3D packing and density rather unfavorable, hence a Madelung energy lower than in other CT crystals. At the same time the CT integral is rather small, but the gap, as estimated by the optical gap (rightmost panel of Fig. 4), is below 1 eV: According to the experiments by Tsutsumi et al. [29], TTB-TCNQ may exhibit good photocarrier generation and transport. In any case, it is worthwhile to investigate the CT complexes of TTB with other electron acceptors which might provide a better overlap and 3D packing.

Acknowledgements

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Supplemental Material for the paper:
Extensive study of the electron donor 1,1,4,4-
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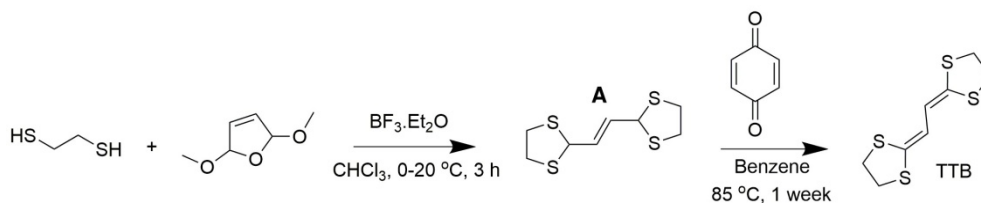
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I. Synthesis of TTB



Ethane-1,2-dithiol (8 mL, 93.5 mmol) and 2,5-dimethoxy-2,5-dihydrofuran (5.2 mL, 41.6 mmol) in 60 mL of dry CH_2Cl_2 were stirred at 0 °C in a 2-neck round bottom flask under Ar. 10 mL of $\text{BF}_3 \cdot \text{Et}_2\text{O}$ was injected very slowly by using a syringe with uniform stirring and the mixture was allowed to warm to 20 °C over a period of 3 h. The precipitate obtained was filtered and washed with diethyl ether. It was further purified with flash column chromatography (silica gel, CH_2Cl_2 :hexane 3:5, v/v) to afford compound **A** as white precipitate (2.4 g, 25%). ^1H NMR (250 MHz, CDCl_3): 5.69 (2H, dd), 5.02 (2H, dd), 3.27 (8H, m).

Compound **A** (3.4 g, 14.4 mmol) and *p*-benzoquinone (7.9 g, 73.1 mmol) were charged into a 250 mL Schlenk flask and degased with Ar. 160 mL of dry benzene was added and refluxed for 1 week. The dark brown solution obtained was diluted with 200 mL toluene and

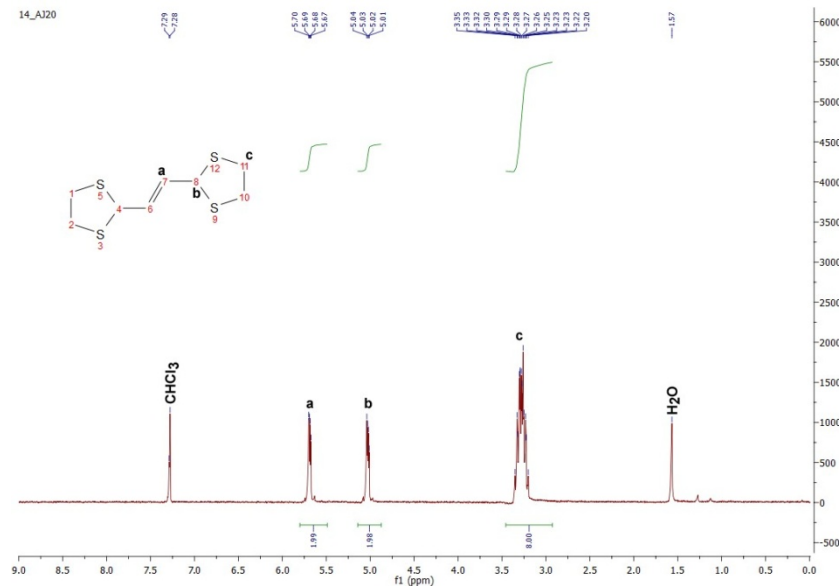


FIG. 1: ^1H NMR of **A** (250 MHz, CDCl_3).

washed with 10% NaOH aqueous solution. The organic layer was dried over MgSO_4 and the solvent was removed under reduced pressure. The obtained crude product was purified by silica column chromatography (CH_2Cl_2 :hexane 2:3, v/v) to yield pure TTB as white crystalline solid (800 mg, 24%). $^1\text{HNMR}$ (400 MHz, CDCl_3): 6.21 (2H, s), 3.40 (8H, m).

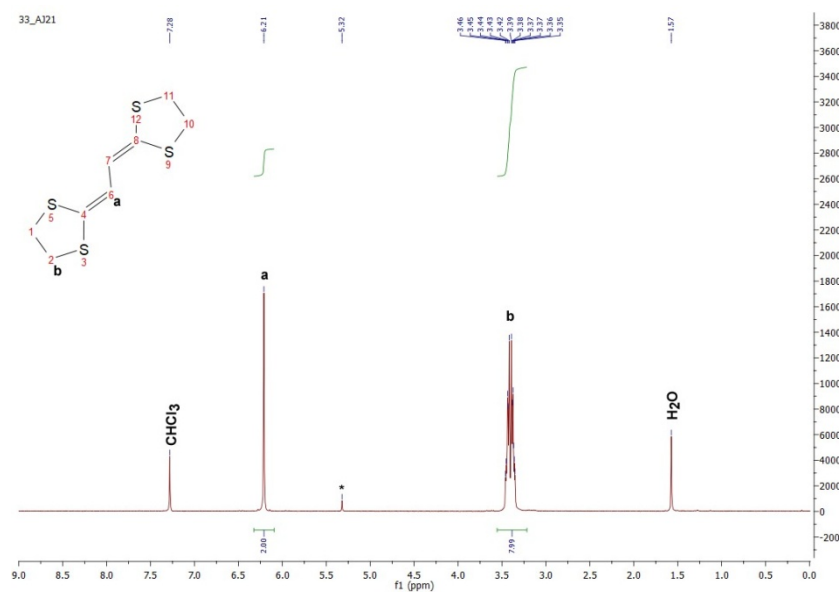


FIG. 2: ^1H NMR of TTB (400 MHz, CDCl_3).

II. Vibrational spectra

Label	TTB			TTB ⁺	
	$\omega_{\text{exp.}}$	$\omega_{\text{scal.}}$	$\omega_{\text{unscal.}}$	$\omega_{\text{scal.}}$	$\omega_{\text{unscal.}}$
$a_g\nu_1$		3042.1	3164.3	3049.9	3172.3
ν_2		3020.3	3141.6	3041.7	3163.8
ν_3	2992	3007.3	3128.0	3030.6	3152.3
ν_4	2969	2962.3	3081.2	2978.0	3097.6
ν_5	2921	2959.3	3078.1	2976.7	3096.2
ν_6	1573	1591.6	1655.5	1541.6	1603.5
ν_7		1450.1	1508.4	1447.3	1505.5
ν_8		1438.8	1496.6	1434.8	1492.4
ν_9	1318	1308.4	1360.9	1290.5	1342.3
ν_{10}	1307	1283.8	1335.3	1289.5	1341.2
ν_{11}	1245	1246.6	1296.6	1255.2	1305.6
ν_{12}	1162	1149.1	1195.3	1223.4	1272.5
ν_{13}	1143	1134.5	1180.0	1149.8	1195.9
ν_{14}		1095.1	1139.0	1099.9	1144.0
ν_{15}	955	954.4	992.7	963.6	1002.3
ν_{16}	931	948.4	986.5	959.7	998.2
ν_{17}		895.9	931.9	939.3	977.0
ν_{18}		845.8	879.7	839.7	873.4
ν_{19}	822	811.1	843.6	828.8	862.1
ν_{20}	684	663.5	690.1	676.4	703.6
ν_{21}		655.5	681.8	645.6	671.5
ν_{22}		643.5	669.3	638.0	663.6
ν_{23}	480	466.5	485.2	463.4	482.0
ν_{24}	463	443.2	461.0	457.7	476.0
ν_{25}	444	427.9	445.1	431.4	448.8
ν_{26}	299	291.7	303.4	244.7	254.5
ν_{27}	229	242.4	252.1	219.2	228.0
ν_{28}		215.9	224.5	216.9	225.6
ν_{29}	155	148.4	154.4	154.9	161.2
ν_{30}		44.7	46.5	89.5	93.1

TABLE I: Experimental, scaled and unscaled calculated frequencies (ω , cm^{-1}) of TTB and TTB⁺ (C_i symmetry). Calculated intensities ($\text{D}^2 \text{Å}^{-2} \text{amu}^{-1}$) are reported only for a_u IR active modes.

Table I
(continued)

Label	TTB TTB ⁺						
	$\omega_{\text{exp.}}$	$\omega_{\text{scal.}}$	$\omega_{\text{unscal.}}$	IR int.	$\omega_{\text{scal.}}$	$\omega_{\text{unscal.}}$	IR int.
$a_U v_{31}$		3051.1	3173.6	0.13979	3058.8	3181.7	0.06192
v_{32}	3003	3020.3	3141.6	0.54849	3041.7	3163.8	0.00219
v_{33}	2956	3007.3	3128.0	0.15225	3030.6	3152.3	0.00287
v_{34}	2920	2962.2	3081.1	1.62965	2978.1	3097.6	0.07510
v_{35}		2959.4	3078.2	0.52615	2976.7	3096.2	0.04336
v_{36}	1524	1541.4	1603.2	4.34586	1447.2	1505.3	0.15533
v_{37}		1450.0	1508.2	0.00306	1434.9	1492.5	0.55480
v_{38}	1415	1438.8	1496.5	0.24332	1380.1	1435.5	12.49079
v_{39}	1273	1282.3	1333.8	2.27983	1290.0	1341.8	0.13625
v_{40}		1270.1	1321.1	0.81498	1285.5	1337.1	6.52965
v_{41}	1241	1242.3	1292.2	0.24307	1250.6	1300.8	0.56710
v_{42}	1147	1140.0	1185.7	0.08545	1150.4	1196.6	0.86802
v_{43}	1104	1095.4	1139.4	0.11832	1100.1	1144.2	0.05113
v_{44}	975	954.2	992.5	0.25573	963.5	1002.1	0.23410
v_{45}		947.3	985.3	0.01378	950.3	988.4	0.19009
v_{46}	845	868.6	903.5	0.26638	909.5	946.0	2.53659
v_{47}	834	831.5	864.9	1.15079	886.6	922.2	0.76855
v_{48}		818.6	851.5	0.58594	838.6	872.3	0.30940
v_{49}	682	663.6	690.3	0.03844	647.4	673.4	0.03556
v_{50}		654.6	680.9	0.33384	639.9	665.6	1.01749
v_{51}		550.9	573.0	0.85310	578.3	601.5	1.66569
v_{52}		471.3	490.2	0.04412	513.4	534.0	0.04378
v_{53}		449.2	467.2	0.13030	454.1	472.3	0.01359
v_{54}		405.2	421.5	0.04778	426.2	443.3	0.18401
v_{55}		401.6	417.7	0.30074	399.7	415.8	0.22625
v_{56}		243.3	253.1	0.16083	217.9	226.7	0.20193

v_{57}	94.6	98.4	0.03493	149.2	155.2	0.05791
v_{58}	62.6	65.1	0.02683	65.4	68.0	0.01564
v_{59}	34.7	36.1	0.16329	50.7	52.8	0.12389
v_{60}	31.7	33.0	0.02761	34.4	35.8	0.00097
