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A complete vibrational study on a potential environmental toxicant agent, the 3,3',4,4'-tetrachloroazobenzene combining the FTIR, FTRaman, UV–Visible and NMR spectroscopies with DFT calculations $\stackrel{\star}{\sim}$

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HIGHLIGHTS

- 3,3',4,4'-Tetrachloroazobenzene was characterized by using spectroscopic techniques.
- Two pairs of conformers of TCAB were theoretically determined in the gas phase.
- B3LYP calculations were used to study the two *cis* and *trans* isomers of TCAB.
- A complete vibrational assignment for 3,3',4,4'-tetrachloroazobenzene was performed.
- The *cis* and *trans* isomers exhibit different structural and vibrational properties.

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ABSTRACT

In this study 3,3',4,4'-tetrachloroazobenzene (TCAB) was prepared and then characterized by infrared, Raman, multidimensional nuclear magnetic resonance (NMR) and ultraviolet-visible spectroscopies. The density functional theory (DFT) together with the 6-31G^{*} and 6-311++G^{**} basis sets were used to study the structures and vibrational properties of the two *cis* and *trans* isomers of TCAB. The harmonic vibrational wavenumbers for the optimized geometries were calculated at the same theory levels. A complete assignment of all the observed bands in the vibrational spectra of TCAB was performed combining the DFT calculations with the scaled quantum mechanical force field (SQMFF) methodology. The molecular electrostatic potentials, atomic charges, bond orders and frontier orbitals for the two isomers of TCAB were compared and analyzed. The comparison of the theoretical ultraviolet-visible spectrum with the corresponding experimental demonstrates a good concordance while the calculated ¹H and ¹³C chemicals shifts are in good conformity with the corresponding experimental NMR spectra of TCAB in solution. The np[®]p^{*} transitions for both forms were studied by natural bond orbital (NBO) while the topological

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properties were calculated by employing *Bader's* Atoms in the Molecules (AIM) theory. This study shows that the *cis* and *trans* isomers exhibit different structural and vibrational properties and absorption bands. © 2014 Published by Elsevier B.V.

Introduction

3,3',4,4'-Tetrachloroazobenzene (TCAB) is a contaminant of dichloroaniline-derived herbicides whose IUPAC chemical name is (3,4-dichlorophenyl)-(3,4-dichlorophenyl)imino-oxidoazanium. Several aniline herbicides yield azobenzenes as products in soil. Soil microorganisms are responsible for the transformation of 3',4'-dichloropropionanilide (propanil) to 3,4-dichloroaniline and subsequently TCAB [1]. Recent studies have demonstrated that mice chronically exposed at dose levels of tetrachloroazobenzene developed a number of neoplastic and nonneoplastic lesions, including carcinoma of the urinary tract [2]. The mechanism of tumor induction is uncertain, but the high frequency of tumors in the proximal urethra of male mice suggests that the neoplasms result from the exposure of a susceptible population of urothelial cells to a carcinogenic metabolite of TCAB [2]. TCAB in itself is not a pesticide [3] but some herbicides are connected directly or indirectly with the compound, hence, the environmental safety of this chemical is extremely important from the viewpoint of human health. The crystal structure of azobenzene [4] and the structural studies of the systems cis and trans-azobenzene were reported [5–7]. The photophysical and photochemical properties of these azobenzene compounds and its derivatives are of industrial interest as light-triggered switches, constituents of erasable holographic data, image storage devices and materials with photomodulable properties, and as a possible basis for a light-powered molecular machine [8]. Computational studies on the potential energy surface (PES), the excited electronic states, the use of quantitative-structure property relationship (QSPR) and artificial neural network (ANN) and, the photoisomerization of the azobenzene compounds and its derivatives were already published [9–12]. So far, the vibrational spectra of TCAB still remain unassigned and, to identify it compound in all the systems by means of vibrational spectroscopy, a complete characterization of the infrared and Raman spectra in solid phase is necessary. Actually, for TCAB there are not theoretical studies on the molecular electrostatic potentials, atomic charges derived from the Merz et al. [13], bond orders, natural atomic charges, force constants and topological analysis. Hence, in this work we prepared and characterized the compound by means of infrared, Raman, multidimensional nuclear magnetic resonance (NMR) and ultraviolet-visible spectroscopies. The structures and vibrational properties for all the isomers of TCAB were studied by using B3LYP level of theory together with the 6-31G^{*} and 6-311++G^{**} basis sets. The optimized geometries and the corresponding frequencies for all the stable conformers of TCAB were calculated by using the same levels of theory. Then, the structural properties and the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy gaps of TCAB were compared and analyzed. The electronic delocalizations for TCAB were calculated by means of the natural bond orbital (NBO) study [15,16] while the topological properties were analysed by employing *Bader's* Atoms in the Molecules theory (AIM) [17,18]. Here, a detailed study of the vibrational spectra of TCAB based on the normal coordinate analysis and the complete assignments of the 66 normal modes of vibration are reported. The corresponding force fields and force constants were obtained using scaling factors [14]. The comparisons of the theoretical ultraviolet-visible spectrum and the calculated ¹H and ¹³C chemicals shifts with the corresponding experimental ones demonstrate a good concordance.

Experimental methods

Synthesis

3,3',4,4'-Tetrachloroazobenzene was obtained according to Mehta and Vakilwala [19] using the following procedure.

To a stirred solution of 3.15 g (0.020 mol) of sodium perborate tetrahydrate in glacial acetic acid (25 mL) was added 0.62 g (0.010 mol) of boric acid and a solution of 1.95 (0.012 mol) of 3,4-dichloroaniline in acetic acid (25 mL). The mixture was heated to 60 °C for 6 h. At this time, no 3,4-dichloroaniline was detected by TLC. The mixture was cooled to room temperature and the yellow product was collected on a Büchner funnel, washed with water to remove acetic acid, dried, and crystallized from dichloromethane. Yield 1.04 g (27%), m.p. = 155.5–156 °C. (Lit. 158 °C).

Equipments

The infrared spectrum of the TCAB solid in KBr pellets from 4000 to 400 cm⁻¹ was recorded on an FTIR GX1 spectrophotometer, equipped with a globar source and a DGTS detector at a resolution of 1 cm⁻¹ and 64 scans. The Raman spectrum (resolution 1 cm⁻¹, 200 scans) was recorded 2000–200 cm⁻¹ with a Bruker RF100/S spectrometer equipped with a Nd:YAG laser source (excitation line 1064 nm, 800 MW power) and a Ge detector.

Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker 300 AVANCE spectrometer at 300 MHz for ¹H and 75 MHz for ¹³C in CDCl₃ solutions containing 0.03 vol.% TMS as internal standard. GC–MS spectrum was recorded on a 5973 Hewlett– Packard selective mass detector coupled to a Hewlett Packard 6890 gas chromatograph equipped with a Perkin–Elmer Elite-5MS capillary column (5% phenyl methyl siloxane, length = 30 m, inner diameter = 0.25 mm, film thickness = 0.25 μ m); ionization energy, 70 eV; carrier gas: helium at 1.0 mL/min. UV spectra were collected on a UV–Visible 160 A Shimadzu spectrophotometer.

Computational details

The potential energy curves associated with rotation around the C1—N12 bond, described by the C2—C1—N12—N13 dihedral angles for the *cis* and *trans* forms of TCAB are observed in Figs. S1 and S2 (Supporting Material) at the B3LYP/6-31G^{*} levels of theory [20,21]. The DFT calculations show, for each form, the presence of two stable conformers with geometries C₁, named Cis-I and Cis-II and Trans-I and Trans-II, respectively. The initials geometries for the two pairs of conformers of TCAB were modeled by means of Gauss-View program [22] and all the structures were optimized at the B3LYP/6-31G^{*} and 6-311++G^{**} levels of theory. The structures and labeling of the atoms for all the structures of TCAB can be seen in Fig. 1. The topological analysis and the NBO calculations for the four structures were performed by using the AIM200 program package [18] and the NBO 3.1 [16] program, as implemented in the Gaussian 03 package [23]. The natural internal coordinates for the cis and trans forms of TCAB are listed in Tables S1 and S2 (Supporting Material) and were defined as those reported in the literature [24–37]. The MOLVIB program [38] was used to transform the resulting force fields in Cartesian coordinates to "natural" internal coordinates. The harmonic force fields for all the forms were

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Fig. 1. Molecular structures of 3,3',4,4' tetrachloroazobenzene and atoms numbering; from C₁ and C₁₁ Cis conformers and C₁ and C₁₁ trans conformer.

evaluated at the B3LYP/6-31G^{*} level following the SQMFF procedure [14]. Then, from resulting SQMFF only the potential energy distribution components (PED) $\ge 10\%$ were considered to perform the final assignment of TCAB.

Results and discussion

Geometry

A comparison of the total energies together with the corresponding dipole moment values for the cis and trans forms, by using both basis sets, is given in Table S3 (Supporting Material). The results show first, that the energies of the two trans forms are significantly lower than the corresponding to the *cis* forms, as observed by Chen and Chieh in a computational study for azobenzene and stilbene [10], and second, that the differences of potential energy between trans-I and trans-II in reference to cis-I and cis-II by using 6-31G^{*} basis set are 0.79 and 3.41 kJ/mol, respectively. Probably, this low energies difference justify the photoinduced isomerization between the two forms, as observed for azobenzene [9]. Note that the high values of the dipole moments for the cis-II and trans-II forms of TCAB could partially explain its stability in solid phase. A similar dependence between energy and dipole moment was also observed in other molecules [39–41]. The calculated geometrical parameters for the cis and trans conformations of TCAB by using both basis sets are summarized in Tables 1 and 2 and, they are compared with the experimental values reported for cis-azobenzene [5], azobenzene [10] and (4-chlorophenyl)quinazolin-4(3H)-one [42] by means of root mean square (rmsd). The rmsd values show that the better bond length and angles values are obtained when the calculated parameters are compared with the azobenzene compound, as expected because it is a similar compound. Note that the N12-C1-C2 and N12-C1-C6 bond angles and the N13-N12-C1-C2 and N13-N12-C1-C6 dihedral angles have different values in both cis conformers. For the structures of the trans conformations a better correlation in the bond angles is observed when their values are compared with the calculated geometrical parameters reported by Chen and Chieh in a

computational study for azobenzene and stilbene [10]. Besides, the B3LYP/cc-pVDZ calculations for those compounds show the coplanarity of the N=N bond in the two *trans* forms because the C-N=N-C dihedral angles are planar and, for this, the interactions of the azo group with the phenyl ring favors the π - π interactions. Probably, these observations only in the two *trans* forms of TCAB justify the energetical stabilities of the two conformations.

Molecular electrostatic potentials and atomic charges

The electrostatic interactions and stabilities of all the TCAB conformers were investigated by using the molecular potentials and the natural atomic charges and the corresponding results are given in Tables S4 and S5, respectively. Note that the higher molecular potentials are observed on the Cl and N atoms of both trans conformers and that the values are approximately the same in the I and II conformers of the two cis and trans forms, as can be seen in Table S4. On the contrary, the NPA charges for the *cis* forms are different from those corresponding to the two trans forms, as observed in Table S5. In this case, we observed on the N atoms the following trend: *cis* I = *cis* II < *trans* I = *trans* II while on the Cl atoms a contrary relation is observed, this is, trans I = trans II < cis I = cis II. The influence of the size of the basis set is notable in both properties and particularly on the Cl and N atoms, thus, the molecular potentials and charges values increase when the 6-311++G^{*} basis set is used while for the remaining atoms a contrary effect in the two properties studied is observed.

The bond orders, expressed by Wiberg's index for all atoms corresponding to the four conformations of TCAB are given in Table S6. Here, the higher values are observed in the N=N— bonds corresponding to the two *cis* forms, being high those values calculated by using $6-311++G^{**}$ basis set. For the Cl atoms a same relation is found, as can be seen in Table S6.

NBO study

The analysis of the stabilization energies is very important in a molecule as TCAB because, as was explained in the introduction

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Table 1

Calculated geometrical parameters for the *cis* conformers of TCAB.

Parameter	Cis-I ^a		Cis-II ^a		Exp ^{b,c} cis	Exp ^{c,d} cis
	6-31G [°]	6-311++G**	6-31G [*]	6-311++G**		
Bond length (Å)						
C1–C2	1,398	1.395	1.399	1.396	1.401	1.410
C2–C3	1.393	1.391	1.394	1.391	1.378	1.378
C3–C4	1.403	1.400	1.403	1.400	1.374	1.374
C4—C5	1.398	1.396	1.398	1.395	1.389	1.389
C5–C6	1.390	1.387	1.389	1.387	1.377	1.377
C6-C1	1.402	1.399	1.400	1.398	1.385	1.385
C14-C15 C15-C17	1.402	1.399	1.402	1.399	1.385	1.385
C17-C21	1.390	1.387	1.309	1.387	1.377	1.377
C21-C19	1.403	1.400	1.403	1.400	1.374	1.374
C19–C16	1.393	1.391	1.393	1.391	1.378	1.378
C16-C14	1.398	1.395	1.398	1.395	1.401	1.410
C1-N12	1.435	1.435	1.434	1.434	1.449	1.449
C14-N13	1.435	1.435	1.434	1.435	1.449	1.449
N12-N13	1.249	1.243	1.249	1.243	1.253	1.253
C3–Cl10	1.745	1.745	1.746	1.746	1.735	1.735
C4CI11	1.744	1.743	1.744	1.744	1.735	1.735
C19-C123	1.745	1.745	1.745	1.745	1./35 1.725	1./35 1.725
021-024	1./44	1./45	1.745	1.745	1.755	1.755
RMSD	0.0033	0.0030	0.0033	0.0030		
RMSD ^d	0.0034	0.0032	0.0034	0.0032		
Pond angle (°)						
C1 - C2 - C3	120 33	120.24	119 98	119 94	119.8	118 7
(2-(3-(4)))	119.82	119.86	120.13	120.12	118.7	1217
C3-C4-C5	119.53	119.54	119.54	119.57	121.7	119
C4–C5–C6	120.76	120.72	120.43	120.43	119.0	120.8
C5-C6-C1	119.62	119.58	119.96	119.88	120.8	120
C6-C1-C2	119.85	119.94	119.86	119.95	120	119.8
N12-C1-C2	115.98	116.14	122.79	122.60		117.3
N12-C1-C6	123.48	123.27	116.68	116.84	122.5	122.5
C1-N12-N13	124.07	124.02	124.28	124.18	121.9	121.9
N12-N13-C14	124.07	124.02	124.05	123.98	121.9	121.9
N13-C14-C15 C14-C15-C17	123.48	123.27	123.54	123.26	122.5	122.5
C14 - C13 - C17 C15 - C17 - C21	120.76	120.72	120.74	120.70	119.0	120
(17 - (21 - (19)))	119 53	119 54	119 55	119.56	121 7	119
C21-C19-C16	119.82	119.86	119.82	119.86	118.7	121.7
C19-C16-C14	120.33	120.24	120.32	120.22	119.8	118.7
C16-C14-N13	115.99	116.14	115.95	116.16		117.3
C16-C14-C15	119.85	119.94	119.83	119.93	120.0	119.8
C2-C3-Cl10	118.66	118.66	118.48	118.50		
C4–C3–Cl10	121.52	121.47	121.39	121.38		
C3-C4-Cl11	121.59	121.55	121.57	121.52		
$C_{2} = C_{4} = C_{11}$	118.88	118.90	118.88	118.90	110.0	110.0
$C_{21} = C_{19} = C_{123}$	121.52	121.47	121.40	121.44	115.5	115.5
C17 - C21 - C124	118.85	118.00	118.85	118.87	1199	1199
C19–C21–Cl24	121.59	121.55	121.60	121.56	11010	11010
RMSD ^b	0 34	0.21	0.46	0.29		
RMSD ^d	0.28	0.27	0.50	0.49		
Dihedral angles (°)						
C1-C2-C3-Cl10	-178.14	-178.04	-179.26	-179.30		
C1–C2–C3–C4	2.98	3.15	0.934	0.845		
C2-C3-C4-Cl11	178.92	178.85	179.24	179.25		
$C_{110} - C_{3} - C_{4} - C_{111}$	0.067	0.080	-0.555	-0.595		
$C_{110} - C_{3} - C_{4} - C_{5}$	-1/9.1/	-1/9.11	1/8.55	1 705		
$C_2 C_3 C_4 C_5$	179 15	179 11	178.85	178 85		
C5-C6-C1-C2	1.815	1.954	-3.63	-3.83		
C5-C6-C1-N12	171.93	172.30	-174.51	-175.06		
N12-C1-C2-C3	-174.57	-174.98	172.00	172.63		
N13-N12-C1-C2	-140.12	-138.93	50.18	50.80		
N13-N12-C1-C6	49.41	50.38	-139.23	-138.22		
C1-N12-N13-C14	10.09	9.69	10.03	9.56		
N12-N13-C14-C15	49.41	50.39	48.80	50.03		
N12-N13-C14-C16	-140.12	-138.93	-140.70	-139.22		
C14-C15-C17-C21	0.844	0.859	0.858	0.845		
C15-C17-C21-C124 C15-C17-C21-C10	1/9.14	1/9.11	1/9.16	1 /9.00		
CIJ-CI/-C2I-CI9	-1.595	-1.000	-1.014	-1./49		

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Table 1 (continued)

Parameter	Cis-I ^a		Cis-II ^a		Exp ^{b,c} cis	Exp ^{c,d} cis
	6-31G [*]	6-311++G**	6-31G [*]	6-311++G**		
Cl24-C21-C19-Cl23	0.067	0.080	0.076	0.191		
Cl24-C21-C19-C16	178.92	178.85	178.90	178.99		
C17-C21-C19-Cl23	-179.17	-179.11	-179.13	-179.03		
C17-C21-C19-C16	-0.321	-0.341	-0.308	-0.238		
C21-C19-C16-C14	2.98	3.15	2.98	3.12		
C19-C16-C14-N13	-174.57	-174.98	-174.61	-175.10		
Cl23-C19-C16-C14	-178.14	-178.04	-178.17	-178.05		

^a This work.

^b From Ref. [10].

^c From Ref. [42]. ^d From Ref. [5].

Table 2

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Calculated geometrical parameters for the trans conformer of TCAB.

Parameter	Trans-I ^a		Trans-II ^a	Exp ^b Trans	
	6-31G*	6-311++G**	6-31G*	6-311++G**	
Bond length (Å)					
C1-C2	1.403	1.401	1.403	1.401	1.385
C2-C3	1.388	1.386	1.388	1.386	1.379
C3-C4	1.408	1.405	1.408	1.405	1.389
C4—C5	1.397	1.394	1.397	1.394	1.368
C5–C6	1.390	1.388	1.390	1.388	1.390
C6-C1	1.400	1.398	1.400	1.398	1.384
C14–C15	1.400	1.398	1.405	1.403	1.385
C15-C17	1.390	1.388	1.386	1.383	1.379
C17–C21	1.397	1.394	1.402	1.399	1.389
C21-C19	1.408	1.405	1.402	1.398	1.368
C19–C16	1.388	1.386	1.393	1.391	1.390
C16-C14	1.403	1.401	1.399	1.396	1.384
C1-N12	1.415	1.415	1.416	1.416	1.433
C14-N13	1.415	1.415	1.416	1.415	1.433
N12-N13	1.260	1.252	1.261	1.252	1.243
C3-C110	1 748	1 748	1 748	1 748	1 735
C4—Cl11	1 743	1 743	1 743	1 743	1 735
C19–Cl23	1 748	1 748	1 746	1 745	1.735
C21-Cl24	1.743	1.743	1.743	1.742	1.735
PMSD			0.0029	0.0022	
RWSD			0.0038	0.0033	
Bond angle (°)					
C1–C2–C3	119.98	119.92	119.98	119.91	119.6
C2-C3-C4	120.07	120.13	120.06	120.13	120.3
C2-C3-Cl10	118.79	118.77	118.79	118.76	
C4–C3–Cl10	121.14	121.10	121.14	121.10	
C3-C4-Cl11	121.40	121.37	121.41	121.38	
C5–C4–Cl11	118.82	118.86	118.81	118.86	
C3–C4–C5	119.78	119.76	119.78	119.76	119.9
C4—C5—C6	120.15	120.18	120.14	120.17	120.4
C5–C6–C1	120.15	120.10	120.17	120.11	119.6
C6-C1-C2	119.87	120.00	119.86	119.90	120.3
N12-C1-C2	124.32	124.20	124.36	124.21	
N12-C1-C6	115.80	115.90	115.78	115.88	115.5
C1-N12-N13	114.82	115.41	114.78	115.34	113.6
N12-N13-C14	114.83	115.41	114.61	115.23	113.6
N13-C14-C15	115.80	115.90	125.07	124.95	
C14–C15–C17	120.15	120.10	119.6	119.53	119.6
C15–C17–C21	120.15	120.18	120.68	120.72	120.3
C17–C21–Cl24	118.82	118.86	118.70	118.71	
C19–C21–Cl24	121.40	121.37	121.52	121.52	
C17–C21–C19	119.78	119.76	119.78	119.77	119.9
C21–C19–Cl23	121.14	121.10	121.58	121.57	
C16–C19–Cl23	118.79	118.77	118.84	118.81	
C21–C19–C16	120.08	120.13	119.58	119.62	120.4
C19–C16–C14	119.98	119.92	120.50	120.42	119.6
C16-C14-N13	124.32	124.20	115.07	115.15	115.5
C16-C14-C15	119.87	119.91	119.87	119,90	120.3
RMSD			0.14	0.18	

Dihedral angles (°)

(continued on next page)

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Table 2 (continued)

Parameter	Trans-I ^a	Trans-I ^a			Exp ^b Trans
	6-31G [°]	6-311++G**	6-31G [°]	6-311++G**	
C1–C2–C3–Cl10	-180	-180	180		
C1-C2-C3-C4	-	-	-		
C2-C3-C4-Cl11	180	180	-180		
Cl10-C3-C4-Cl11	-	-	-		
Cl10-C3-C4-C5	180	180	180		
C2-C3-C4-C5		-	-		
Cl11-C4-C5-C6	180	180	-180		
C5-C6-C1-C2	-	-	-		
C5-C6-C1-N12	180	180	-180		
N12-C1-C2-C3	180	180	180		
N13-N12-C1-C2	0.036	0.008	-		
N13-N12-C1-C6	-180	-179.99	-180		
C1-N12-N13-C14	180	-179.99	179.99		
N12-N13-C14-C15	179.99	180	-		
N12-N13-C14-C16	-	-	180		180
C14-C15-C17-C21	-	-	-		
C15-C17-C21-Cl24	180	-180	-180		
C15-C17-C21-C19	-	-	-		
Cl24-C21-C19-Cl23	0.005	-	-		
Cl24-C21-C19-C16	-180	-180	-180		
C17-C21-C19-Cl23	-180	-180	-180		
C17-C21-C19-C16	0.004	-	-		
C21-C19-C16-C14	-	-	-		
C19-C16-C14-N13	180	-180	-180		
Cl23-C19-C16-C14	180		180		

^a This work.

^b From Ref [10].

section, they have photochemical properties of industrial interest as light-triggered switches [8,9]; hence the two pairs of TCAB conformers were studied by means of NBO calculations [16]. Tables S7 shows the second order perturbation energies $E^{(2)}$ (donor \rightarrow acceptor) corresponding to the most important delocalization for all the conformers of TCAB. For both forms, four contributions of the stabilization energies are observed by using both basis sets, $\Delta ET_{\pi \rightarrow \pi^*}$, $\Delta ET_{LP \rightarrow \sigma^*}$, $\Delta ET_{LP \rightarrow \pi^*}$ and $\Delta ET_{\pi^* \rightarrow \pi^*}$ of which the $n \rightarrow \sigma^*$ and $n \rightarrow \pi^*$ contributions favors to the two *cis* forms while the two remaining favors to the *trans* forms. This analysis justify clearly the stabilities of the two *trans* forms because the planarity of the C—N=N—C dihedral angles produce a higher total electron delocalization and, as consequence favors the $\pi \rightarrow \pi^*$ type interactions and the energetical stabilities of the two *trans* conformations. Table S7 shows that the C atoms of the two rings in all the conformers



Fig. 2. (a) Comparisons between the experimental infrared spectra of 3,3',4,4'tetrachloroazobenzene with the corresponding theoretical at B3LYP/6-31G^{*} for: (b) *Cis* I conformer, (c) *Cis* II conformer, (d) *Trans* I conformer and, (e) *Trans* II conformer. together with the N12 and N13 atoms are strongly conjugated by the electron density $LP \rightarrow \pi^*$ and $LP \rightarrow \sigma^*$ donations where the LP transitions are p orbitals of the C, N12 and N13 atoms. These mechanisms explain the existence of a relatively high occupancy of π^* orbitals and of the $\pi^* \rightarrow \pi^*$ transitions. On the other hand, probably the predicted $\pi^* \rightarrow \pi^*$ transitions due to the shorter lifetime of the



Fig. 3. (a) Comparisons between the experimental Raman spectra of 3,3',4,4'tetrachloroazobenzene with the corresponding theoretical at B3LYP/6-31G^{*} for: (b) *Cis* I conformer, (c) *Cis* II conformer, (d) *Trans* I conformer and, (e) *Trans* II conformer.

Table 3

Observed and calculated wavenumbers (cm⁻¹) and assignment for TCAB conformers.

By solut Resignment* SQM* Asignment* SQM* Asignment* SQM* Asignment* 1118 100 Cr5-H18 1100 Cr5-H18 1111 Cr2-H7 1114 Cr2-H7 118 1007 Cr5-H18 1101 Cr2-H7 1104 Cr5-H18 1100 Cr5-H18 118 1007 Cr5-H18 1008	Experiment	al ^a	Cis I		Cis II		Trans I		Trans II	
118	IR solid	Raman	SQM ^b	Assignment ^a	SQM ^b	Assignment ^a	SQM ^b	Assignment ^a	SQM ^b	Assignment ^a
Set Bes V Sino VCS-H18 Sino VCS-H18 Sino VCS-H18 Sino VCS-H20 Sino VCS-H20 <td>3118 vw</td> <td></td> <td>3100</td> <td>vC6—H9</td> <td>3105</td> <td>vC2—H7</td> <td>3113</td> <td>vC2—H7</td> <td>3114</td> <td>vC2—H7</td>	3118 vw		3100	vC6—H9	3105	vC2—H7	3113	vC2—H7	3114	vC2—H7
3889 ····································			3100	vC15-H18	3100	vC15-H18	3113	vC16—H20	3110	vC15-H18
Set h Singer VCS-H8 Singer VC1-H22	3089 w		3097	vC16-H20	3097	vC16-H20	3099	vC5—H8	3102	vC16—H20
3082 m 3067 v:C3-H2 3067 v:C3-H2 3067 v:C3-H2 3068 v:C3-H2 3068 v:C3-H2 3068 v:C3-H2 3068 v:C3-H2 3068 v:C3-H2 3068 v:C3-H2 3067 v:C3-C1 307 v:C3-C1 307 v:C3-C1 307 v:C3-C1 307 v:C3-H2 3067 v:C3-H2			3097	vC2—H7	3097	vC5—H8	3099	vC17—H22	3100	vC5—H8
3062 3071 VV 3070 v(17)-H32 3083 v(15)-H18 3087 v(15)-H18 <th< td=""><td>3082 sh</td><td></td><td>3087</td><td>vC5—H8</td><td>3087</td><td>vC17—H22</td><td>3087</td><td>vC6—H9</td><td>3088</td><td>vC17—H22</td></th<>	3082 sh		3087	vC5—H8	3087	vC17—H22	3087	vC6—H9	3088	vC17—H22
1578 vv 1577 158 vc13-c17 158 vc13-c17 158 vc13-c17 158 vc3-c6 1558 vv 157 vc3-c6 1531 vc3-c6 1531 vc3-c6 1531 vc3-c6 1531 vc3-c6 1532 vc3-c6 1533 vc3-c7 1533 vc3-c7 1533 vc3-c7 1533 vc3-c6 1533 vc3-c6 1533 vc3-c6 1533 vc3-c6 1533 vc3-c6 1533 vc3-c6 <td< td=""><td>3062 w</td><td>3071 vw</td><td>3087</td><td>vC17—H22</td><td>3083</td><td>vC6—H9</td><td>3087</td><td>vC15—H18</td><td>3087</td><td>vC6—H9</td></td<>	3062 w	3071 vw	3087	vC17—H22	3083	vC6—H9	3087	vC15—H18	3087	vC6—H9
	1578 vw	1577 m	1587	vC5—C6	1588	vN12—N13	1586	vC15-C17	1587	vC15-C17
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	1578 vw	1577 m	1577	vC15-C17	1577	vC5-C6	1581	vC5—C6	1583	vC5-C6
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	1558 m	1568 sh	1555	vC1-C2; vC16-C14	1552	vC6-C1	1565	vC6-C1; vC14-C15	1564	vC6C1
	1558 m		1540	vC6-C1; vC14-C15	1545	vC1-C2;	1556	vC16-C14	1552	vC16-C14
	1466 vs	1474 m	1537	vN12-N13	1538	vC14-C15	1484	vN12-N13	1487	vN12-N13
	1456 sh	1445 s	1455	$\beta(CT/-H22)$	1456	$\beta(CT/-H22)$	1453	β(CT/H22)	1458	$\beta(C17-H22)$
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	1456 SN	1445 S	1455	$\beta(C5-H8)$	1455	$\beta(C5-H8)$	1448	$\beta(CS - H\delta)$	1202	$\beta(CS - H8)$
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	1202 S	1378 111	1277	vC19-C10	1274	vC19-C10	1202	VC2-C3	1202	vC2-C3
	1373 SII 1287 W	1200 104	1377	vC2-C3	1374	vC2-C3	1385	vC19-C10	1200	vC13-C10
	1270 vov	1268 104	1260	$vC4 - C5 \cdot vC17 - C21$	1270	vC3-C4	1205	vC17_C21	1290	vC3-C4
1244 1248 1C16-1200 1248 RC16-1200 1246 RC16-1200 1246 RC16-1200 1246 RC16-1200 1169 w 1142 (1C5-118) 1138 (C16-120) 1153 vC1-N12 1155 vC1-N12 1132 m 1134 vC1-N12 1134 vC1-N12 1135 vC1-N12 1136 1120 n 1130 vC1-N12 1134 vC1-N12 1137 vC1-N12 VC1-N12 1120 n vC1-N12 1138 vC1-N12 1128 VC1-P19 1102 VC1-P12 925 VC1-P19 </td <td>1254 w</td> <td>1252 w</td> <td>1205</td> <td>B(C2 - H7)</td> <td>1203</td> <td>в(С2—H7)</td> <td>1258</td> <td>vC4-C5</td> <td>1256</td> <td>vC4C5</td>	1254 w	1252 w	1205	B(C2 - H7)	1203	в(С2— H7)	1258	vC4-C5	1256	vC4C5
1209 1132 1152 1152 1152 1152 1153 1153 1153 1153 1153 1154 1154 1154 1155 1134 1134 1134 1134 1134 1134 1134 1134 1134 1134 1134 1134 1134 1134 1134 1134 1134 1134 1134 1134 1134 1134 1134 1134 1134 1134 1134 1134 1134 1134 1134 1134 1134 1134 1134 1135 1135 1135 1135 1135 1135 1135 1135 1135 1135 1135 1135 1135 1135 1135 1135 1135 1135 1135 1135 1135 1135 1135 1135 1135 1135 1135 1135 1135 1135 1135 1135 1135 1135 1135 1135 1135 1135 1135 1135 1135 1135 <th< td=""><td>1254 W</td><td>1252 W</td><td>1240</td><td>$\beta(C16-H20)$</td><td>1232</td><td>$\beta(C16-H20)$</td><td>1236</td><td>B(C16-H20)</td><td>1236</td><td>B(C16-H20)</td></th<>	1254 W	1252 W	1240	$\beta(C16-H20)$	1232	$\beta(C16-H20)$	1236	B(C16-H20)	1236	B(C16-H20)
	1209 s	1213 vw	1152	B(C6-H9)	1152	$\beta(C15 - H18)$	1193	vN13-C14	1196	vN13-C14
	1169 vw	1169 vs	1142	β(C15-H18)	1132	vC15-C17	1153	vC1-N12	1155	vC1-N12
	1132 m	1138 vw	1134	vC1-N12	1134	B(C6-H9)	1126	$\beta(C15-H18)$	1129	$\beta(C15-H18)$
	1120 s	1124 w	1130	vN13-C14	1128	vN13-C14	1125	β(C6—H9)	1125	B(C6—H9)
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	1077 vw	1105 sh	1106	vC21-C19	1109	vC3-C4	1103	vC3-C4	1104	vC17-C21
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$			1106	vC4-Cl11	1106	vC21-C19	1102	β(C2—H7)	1102	β(C2—H7)
	1028 s	1029 vw	1024	βR_1 (A1)	1025	βR_1 (A1)	1023	$\beta R_1 (A2)$	1023	$\beta R_1 (A2)$
958 958 950 y (c1=1H8 955 y (c1=H8 977 y (c1=H18 978 y (c1=H12) 962 y (c1=H12) 962 y (c1=H12) 963 y (c1=H12) 964 y (c1=H12) 964 y (c1=H12) 963 y (c1=H12) 973 y (c1=H12	1028 s		1023	$\beta R_1 (A2)$	1023	$\beta R_1 (A2)$	1022	$\beta R_1 (A1)$	1022	$\beta R_1 (A1)$
939 939 950 7C6-H9 949 7C17-H22 960 7C6-H9 962 7C6-H9 995 m 995 m 7C2-H7 886 7C2-H7 980 7C1-C2 984 7C1-C2 984 7C1-C1 986 7C1-C1 986 7C1-H20 995 7C1-H20 895 7C1-H20 805 7C1-H20 805	958 vw	958 vw	950	γC15—H18	955	γС6—Н9	963	γC15—H18	977	γC15—H18
906 97C16-H20 904 97C1-C2 948 97C1-C2 884 s 894 s 862 3(C14-H13) 871 vC1-H7 925 vC16-H20 909 vC16-H20 886 sh 800 7C5-H8 844 vC5-H18 837 vC17-H22 839 vC1-H20 839 vC1-H20 839 vC1-H22 839 vC	939 vw	939 vw	950	γC6—H9	949	γC17—H22	962	γC6—H9	962	γС6—Н9
	905 m		906	γC16—H20	904	γC16—H20	960	vC1-C2	948	vC1-C2
	894 s		894	γC2—H7	888	γC2—H7	927	γС2—Н7	926	γC2—H7
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	886 sh		862	δ(C14-N13)	871	vC1-N12	925	γC16—H20	909	γC16—H20
			840	γС5—Н8	844	γС5—Н8	887	vC3—Cl10	887	vC14—C15
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	823 s		831	vC3–Cl10	829	γС5—Н8, γС15—Н18	837	γC17—H22	839	γC17—H22
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	814 w		825	γC17—H22	827	γC15—H18	833	γС5—Н8	834	γС5—Н8
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	794 w	795 vw	791	δN12-C1	784	δ(C14–N13)	763	βR_2 (A1)	777	βR_2 (A1)
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	705 m	693 vw	691	$\tau R_1(A1)$	693	τR_1 (A1)	695	βR_3 (A1)	695	τR_1 (A1)
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	690 m		686	βR_3 (A1)	682	$\beta R_3 (A1)$	695	τR_1 (A1)	686	βR ₃ (A1)
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	671 vw	673 vw	675	$\beta R_3 (A2)$	679	$\beta R_3 (A2)$	682	$\tau R_1 (A2)$	681	$\tau R_1 (A2)$
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	671 vw		669	$\tau R_1 (A2)$	673	$\tau R_1 (A2)$	674	$\beta R_3 (A2)$	679	$\beta R_3 (A2)$
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	656 W		615	γC3-CΠ0	616	γC19=C123	644	VC4CITI	644	VC4CITI
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	606 W		605	VC21-CI24	613	vC4-CITT	507	$\gamma(N12-C1)$	606	$\gamma(N12-C1)$
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	EC1	E 40	604 E42		501 541	vC2 C110	509	S(C14, N12)	500	o(C14 - N13)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	544 yrs	546 VW	545	1 M	525	τP (A2)	511	0(C14 - N15)	517	$\gamma(113-C14)$
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	102 vm	462 104	34Z 456	$\gamma(10_{12}-01)$	323	$r_{2}(AZ)$	311 451	$P(C_2 - C_{124})$	J17 454	vC10-Cl22
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	458 100	402 VW	450	τR_{a} (A2)	437	τR_{o} (A1)	431	$\tau R_{\rm e}$ (A2)	445	$\tau R_{\rm e}$ (A2)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	442 vw	152 110	440	$\tau R_2 (A1)$	437	$\tau R_2 (A2)$	444	vC19-C123	439	$\tau R_2 (A1)$
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	430 vw	436 vw	435	τR_2 (A2)	435	vC3-Cl10	438	$\tau R_2(A1)$	434	vC3-Cl10
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	415 vw	388 w	404	$\gamma C4 - C111$	415	B(C3-C110)	392	B(C14-N13)	422	$\beta(C3-C110)$
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	393 vw	372 vw	379	$\beta(C3-C 10)$	395	$\tau N = N$	385	$\beta R_2(A1)$	373	$\gamma C4 - C111$
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	391 vw	365 vw	359	$\beta R_2 (A1)$	352	$\beta R_2 (A1)$	374	γ C 4– C l11	356	$\beta R_2 (A2)$
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	374 m	335 vw	331	βR_2 (A2)	339	βR_2 (A2)	345	γC21—Cl24	337	γC21—Cl24
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		296 vw	293	γC21-Cl24	292	γC4—Cl11	308	β(C19—Cl23)	305	β(C19–Cl23)
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		290 vw	286	γC21—Cl24	285	γC21—Cl24	218	$\beta R_2 (A2)$	221	γC19—Cl23
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$		217 vw	213	β(C14—N13)	215	β(C14—N13)	213	γC19—Cl23	213	β(C21–Cl24)
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$			203	β(C21–Cl24)	202	β(C21–Cl24)	200	β(C21–Cl24)	201	β(C4–Cl11)
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$		180 vw	198	β(C4Cl11)	198	β(C4Cl11)	200	vC19-Cl23	194	γC3-Cl10
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$			182	β(C19–Cl23)	189	β(C19–Cl23)	180	γC3—Cl10	181	β(C1-N12)
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		170 vw	164	γC19—Cl23	166	γ(N13–C14)	156	τC2-C1-N12-N13	146	τC2-C1-N12-N13
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		137 vw	135	τR_2 (A1)	133	τN=N	133	$\tau R_2(A2)$	142	β(C14—N13)
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		120 vw	113	β(C1-N12)	103	β(C1-N12)	121	β(C1-N12)	125	$\tau R_2 (A2)$
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		109 vw	84	τR_2 (A2)	83	τR_2 (A1)	64	τR_2 (A1)	67	τR_2 (A1)
22 τC2C1N12N13 24 τC2C1N12N13 30 τN=N 30 τN=N 20 τC16C14N13N12 20 τC16C14N13N12 15 τC16C14N13N12 13 τC16C14N13N12			35	γ(N13–C14)	31	γ(N12–C1)	45	δN12-C1	44	δN12—Cl
20 TC16-C14-N13-N12 20 TC16-C14-N13-N12 15 TC16-C14-N13-N12 13 TC16-C14-N13-N12			22	τC2-C1-N12-N13	24	τC2-C1-N12-N13	30	τN=N	30	τN=N
			20	τιι6ι14Ν13Ν12	20	τιι6ι14Ν13Ν12	15	τιι6	13	τc16-C14-N13-N12

Abbreviations: ν, stretching; β, deformation in the plane; γ, deformation out of plane; wag, wagging; τ, torsion; βR, deformation ring τR, torsion ring; ρ, rocking; τw, twisting; δ, deformation; Butt, butterfly; a, antisymmetric; s, symmetric; A1, Ring 1; A2, Ring 2.

^a This work.

^b From scaled quantum mechanics force field at B3LYP/6-31G^{*}.

excited species in solution cannot be detected in this study since electronic transitions are more rapid than molecular vibrations or possibly because the absorption maximum is outside the spectral range of 240–640 nm, as observed in Fig. S3.

AIM analysis

The electronic distribution on the atoms corresponding to all the conformers of TCAB were analysed by means of Bader's charge electron density topological analysis [17]. The calculated electron density, (ρ) and the *Laplacian* values, $\nabla^2 \rho(r)$ in the ring critical points (RCPs) for the four structures are shown in Table S8. The results show for the two *trans* forms the higher topological properties values by using 6-31G^{*} basis set while when increase the size of the basis set at 6-311++G^{**} increase only the (ρ) and $\nabla^2 \rho(r)$ values for the two *cis* forms, as observed in Table S6. The analysis shows a slightly dependence of the topological properties with the size of the basis set, stabilizing in general to the *trans* conformers of TCAB. Then, the topological properties in part explain the different stabilities between the *cis* and *trans* structures of TCAB.

Vibrational analysis

This analysis was performed taking into account the energetical stabilities of the two pairs of conformers of TACB and the small difference energies among them. This way, the vibration normal modes corresponding to the two pairs of conformers were considered in the study. The comparison of the calculated infrared and Raman spectra for TCAB by using B3LYP/6-31G^{*} theory level with the corresponding experimental ones demonstrate a good correlation, as observed respectively in Figs. 2 and 3. Note that the strong bands between 1500 and 1000 cm⁻¹ in the experimental IR spectrum are justified by the presence of both trans forms while probably in this region these bands overlap those bands attributed to the cis forms. On the other hand, the bands observed in the higher and lower wavenumbers regions in the Raman spectrum are probably attributed to the two cis forms and, this way, those bands justify the existence of both forms in the solid phase. The two pairs of conformations of TCAB have C_1 symmetries and 66 normal vibration modes where all the vibrations are IR and Raman active. The assignment of the experimental bands to the expected normal vibration modes were made on the PED $\ge 10\%$ contributions, by using of symmetry coordinates and taking into account the assignments for similar compounds [10,29-32,37,39]. Table 3, Tables S9 and S10 show the experimental and calculated frequencies, potential energy distribution based on the 6-31G^{*} basis set, and assignment for the two pairs of conformers of TCAB. We considered the B3LYP/ 6-31G^{*} calculations because the used scale factors are defined for this basis set. The SQM force fields for this compound can be obtained upon request.

Assignments

C—*H* modes. The IR bands between 3118 and 3062 cm⁻¹ (Fig. 2 and Table 3) can be assigned to the CH stretchings modes of both rings, as predicted by calculations. Taking into account the assignments for compounds containing CH groups [10,29-32,36,37,43,44] the IR bands between 1466 and 1169 cm⁻¹ are assigned to the CH in-plane deformation modes for the two pairs of conformers while the corresponding out-of-plane deformation modes are associated to the IR bands between 958 and 814 cm⁻¹.

CCl modes. The C–Cl stretching modes are predicted in the expected region [43,44] and, for this, they can be clearly assigned to the bands between 606 and 442 cm⁻¹. For *cis* and *trans* forms



Fig. 4. Experimental in ethanol solution (upper) and theoretical (bottom) ultraviolet-visible spectrum of 3,3',4,4' tetrachloroazobenzene.

of TCAB, the C—Cl in-plane deformation modes were predicted at lower wavenumbers in relation to the corresponding out-of-plane deformation modes, hence they were assigned in agreement with the calculations and, as observed in Table 3.

Skeletal modes. In accordance with the lower calculated N12=N13 distances for the *cis* I and II forms (1.249 and 1.243 Å, respectively) the frequencies for the corresponding N=N stretching modes are predicted by calculations at higher wavenumbers than the trans stretching modes (1.261 and 1.252 Å), hence, they were assigned to the Raman bands at 1577 and 1474 cm⁻¹, where the latter band is observed as intense in the IR spectrum at 1466 cm⁻¹. Those stretching modes for the trans forms are also assigned at 1466 cm⁻¹, because both modes are predicted at 1484 and 1487 cm⁻¹. The N–C stretching modes for the *trans* and *cis* forms of TCAB are easily assigned to the strong IR bands at 1209 and 1120 cm⁻¹, respectively. The ring stretching modes for both forms of TCAB are assigned to the IR and Raman bands respectively at 1558 and 1577 cm⁻¹, as indicated in Table 3. The remaining C–C stretching modes are assigned as predicted by SQM calculations. On the other hand, the three phenyl ring deformations and torsions are assigned in the expected regions, as observed in molecules containing similar rings [10,29-32,36,37,43,44] and as indicated in Table 3.

Force field

Table 4 shows the calculated forces constants for the two pairs of conformers of TCAB. The values were calculated by means of the SQM methodology [14] with the Molvib program [38]. Note that in all the forces constants there are a certain dependence of the values with the size of the basis set diminishing slightly when increase the basis set of 6-31G^{*} at 6-311++G^{**}. The analyses show that the f(N=N) force constants for the cis forms of TCAB have higher values than the corresponding to the trans forms, in accordance with the lower calculated N12=N13 distances which. in the cis I and II forms are respectively 1.249 and 1.243 Å while in the trans I and II forms the values are approximately 1.261 and 1.252 Å. On the contrary, the higher C1-N12 and C14-N13 distances in both cis conformers justify the differences in their f(vC–N) force constant values being highest in the *trans* forms, as can be seen in Table 4. On the other hand, the different C19–Cl23 and C21–Cl24 distances values for all the conformers

Force constant	Cis TCAB				Trans TCAB			
	Cis I		Cis II		Trans I		Trans II	
	6-31G [°]	6-311++G**	6-31G [*]	6-311++G**	6-31G [°]	6-311++G**	6-31G [*]	6-311++G**
f(C—N)	4.001	3.903	4.016	3.908	4.958	4.847	4.948	4.838
f(N-N)	10.296	10.195	10.293	10.191	9.583	9.558	9.583	9.558
f(C-C) _{ring}	6.436	6.320	6.444	6.329	6.447	6.325	6.446	6.324
f(C—Cl)	3.456	3.400	3.455	3.399	3.430	3.374	3.443	3.388
<i>f</i> (C—H)	5.253	5.169	5.254	5.169	5.261	5.186	5.273	5.188

 Table 4

 Comparison of scaled internal force constants for TCAB conformers.

Units are mdyn Å⁻¹ for stretching and stretching/stretching interaction and mdyn Å rad⁻² for angle deformations.

of TCAB justify the values of the corresponding f(C-CI) force constants. Here, the lower values in the f(N=N) and $f(C-C)_{ring}$ force constants for the *trans* forms are probably related to the strong $\pi \rightarrow \pi$ delocalizations observed by NBO analysis due to the planarity of those two forms.

HOMO-LUMO energy gap

The presence of lone pairs on the two N atoms and of four electronegative Cl atoms conifer to TCAB interesting structural and electronic properties, as reveled by above studies. To study the role of those two atoms on the reactivity of TCAB the frontier molecular HOMO and LUMO orbitals [45] for all the conformers were calculated at different levels of theory and compared among them, as observed in Table S11. The results clearly show that: (i) both frontier orbitals are localized on the rings, (ii) the energies gap follows the trend: *cis* I > *trans* II > *trans* I > *cis* II and (iii) the large gap energy makes TCAB kinetically inert because present a good stability and a high chemical hardness.

Electronic spectrum

A comparison between the electronic spectrum of TCAB registered in ethanol solution with the corresponding calculated for the two *cis* and *trans* forms at B3LYP/6-31G^{*} level of theory can be seen in Fig. 4. The graphical show that the cis and trans isomers exhibit different absorption bands. Thus, the theoretical calculations by using both basis sets predict for the *cis* forms four bands located at 490 nm (2.5324 eV) with an oscillator strength f = 0.0607, at 278 nm (4.4614 eV) with f = 0.1283, at 200 nm (6.2282 eV) with f = 0.3658 and at 154 nm (8.0212 eV) with f = 0.1345, while for the *trans* forms the theoretical calculations by using 6-31G^{*} basis set predict four bands while when the other basis set is used only three bands are predicted. In the first case, the bands are located at 357 nm (3.4738 eV) with an oscillator strength f = 0.8978, at 239 nm (5.1812 eV) with f = 0.1527, at 188 nm (6.5686 eV) with f = 0.2437 and, at 149 nm (8.3075 eV) with f = 0.0840. On the other hand, the measured experimental show only two bands, an intense and broad centered in approximately 335 nm and other band at 445 nm. The deconvolution of the first experimental band produces three bands at 293, 335 and 361 nm that are shifted in relation to those calculated using TD/B3LYP calculations. These bathochromic shifts found for trans molecules, as compared with the *cis* forms, were also observed by Chen and Chieh [10] in the azobenzene compounds and they have attributed that variation to a better conjugated effect for the trans forms in reference to the cis forms. The four experimentally bands observed were assigned to the chromophores present in the molecule, being higher the $n \rightarrow \pi^*$ transitions for the *cis* forms and the $n \rightarrow \pi^*$ transitions for the *trans* forms, in accordance with reported data for azobenzene [10] and with the results of the NBO calculations performed here.

Conclusions

We have synthesized and characterized TCAB by infrared, Raman, multidimensional nuclear magnetic resonance (NMR) and ultraviolet-visible spectroscopies. The assignments of the 66 normal modes of vibration corresponding to both *cis* and *trans* isomers of the compound are reported. The theoretical structures of two cis and *trans* forms of TCAB were determined by using the 6-31G^{*} and 6-311++G^{***} basis sets. The molecular electrostatic potentials, atomic charges and bond orders support the high stability of the trans forms together with the NBO studies, which suggest that the electronic transitions of the two *cis* forms are $n \rightarrow \pi^*$ transitions while for the *trans* forms are $n \rightarrow \pi^*$ and $\pi^* \rightarrow \pi^*$ transitions. Thus, the topological parameters and the main delocalization energies favor to the trans forms. The calculated highest occupied molecular orbital (HOMO)-lowest unoccupied molecular orbital (LUMO) energy gaps for the four conformations of TCAB follow the trend: cis I > trans II > trans I > cis II. The SQM/B3LYP/6-31G^{*} force field for the two pairs of conformers of TCAB were obtained together with the more important force constants. This study shows that the cis and trans isomers exhibit different structural and vibrational properties and absorption bands. Additionally, the size of the basis set reveals the importance of it in all the studied properties.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.saa.2014.07.032.

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