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ELECTRONIC STRUCTURE AND SPECTRA OF TETRATHIOTETRACENE AND RELATED MOLECULES

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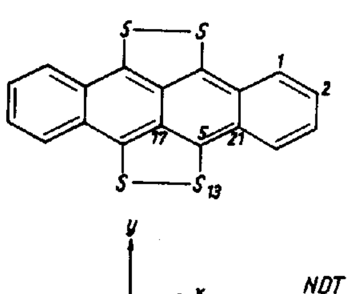
Abstract—The electronic spectra of tetrathiotetracene (TTT) and of its mono- and dipositive ions have been calculated by the Pariser–Parr–Pople (PPP) method. Furthermore, the band polarizations of the first two bands of TTT have been measured. A reasonable band assignment is given using a new set of PPP parameters based on spectral data of a naphthalene derivative containing similar typical weak S–S bond. Other physical parameters as ionization potential, disproportionation energy, S–S bond length and net π-charges are discussed.

Recently high interest arose concerning the physicochemical properties of organic charge transfer salts.[1] An important group of these materials are the complexes of the donor molecule tetrathiotetracene (= naphthaceno[5,6-cd:11,12-c'd']bis[1.2]dithiolane, TTT) forming highly conducting salts with different acceptors (halogens,[2] TCNQ,[3] $NiS_4C_4H_4$,[4] particularly the iodides have high conductivities).[5] In order to determine the complex physical properties of these materials, a necessary step is the elucidation of the molecular physics of the constituting molecules. A molecular orbital (MO) study seems to be an appropriate tool for the theoretical evaluation of the important molecular parameters like electron–electron repulsion parameter,[6] charge distribution, spectral data, etc. The aim of this paper is to report on our investigations related to TTT, TTT^+ and TTT^{2+}.

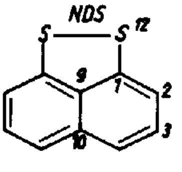
Since in aromatic molecules, as in TTT, the π-electron properties are dominating, we attempted to treat the TTT molecule and its mono- and dipositive ions in π-electron approximation using the PPP method.[7] Many studies of this kind have been published for molecules containing one S atom.[8–13] Only a limited number of calculations have been performed for ring molecules containing S–S bonds,[14] and the results are poorer than usually expected for the PPP method.

In addition to TTT, the following molecules have been also involved in our calculations: 1,8-naphthalene-disulphide (= naphtho[1,8-cd]-1,2-dithiol, NDS) and 1,8-naphthalene-dithiol (NDT). A detailed study of these molecules seems to be useful not only because of the parameterization problems but also in order to obtain information on the assignment of the longest wavelength transition of TTT and on the role of S–S bond in determining the molecular properties.

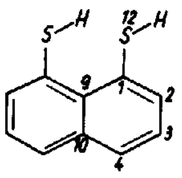
TTT



NDS



NDT



EXPERIMENTAL

The band polarizations of tetrathiotetracene have been determined experimentally from polarized absorption spectra in nematic liquid crystals as anisotropic solvents.

The experimental cells consisted of two SnO_2-coated quartz-plates held on a distance of 500 μm by a Teflon spacer. The alignment of the nematic samples has been achieved by a rubbing procedure and by an electric field. The spectra have been measured with a Cary 17 spectrophotometer with linear polarized light. The method, which has been described elsewhere[15] is based on the fact that solute molecules in nematic solvents are preferably oriented with the axes of the greatest polarizability (usually the long molecular axes) parallel to the optical axis of a nematic layer. If $D_\parallel$ and $D_\perp$ are the optical densities, measured with the electric vector of the light parallel and perpendicular to the optical axis of the sample, the (corrected) dichroic ratio, R =

$(D_\parallel \cdot n_\parallel)/(D_\perp \cdot n_\perp)$ ($n_\parallel$ and $n_\perp$ are the refractive indices of the nematic phase) provides information on the polarizations of the electronic transitions of the solute molecules. The dichroic ratios found in two nematic solvents, N9 (Merck) (mixture of nematic esters) and K21 (BDH) (*p*-n-heptyl-*p*'-cyano-biphenyl) are 0.628 (N9) and 0.599 (K21) for the first band and 3.637 (N9) and 3.898 (K21) for the second band, respectively. From the R-values one can see that the band centered around 14,200 cm^{-1} is polarized perpendicular and the band at 21,200 cm^{-1} is polarized parallel to the long molecular axis of tetrathiotetracene.

Tetrathiotetracene was synthetized by Dr. K. Ritvay-Emandity.[28]

Method of calculation

The PPP method has been used in its standard form. The ground state π-electron properties, singlet–singlet transition energies, and the magnitude and direction of transition moments have been calculated. The two-center repulsion integrals ($\gamma_{\mu\nu}$) have been evaluated by the Mataga–Nishimoto approximation.[16] A limited configuration interaction (CI) treatment using generally 36 single excited configurations has been included. The parameters giving best agreement between calculated and experimental transition energies (see second column of Table 1) were worked out on both NDS and TTT. For TTT^+ the Longuet-Higgins and Pople-type open shell SCF–CI version of the method was used.[17]

We have started with parameters which give satisfactory results for benzenethiols and thiophene derivatives[18] (see column 1 of Table 1 except β_{S-S} for which we could find only one literature value: -1.0 eV[15]). The experimental spectrum of neither NDS nor TTT could be reproduced with this set, even if we changed β_{S-S} in the 0 to -2.4 eV range. (In the best case the first transition energy was by 1 eV larger than the experimental value.)

In the subsequent calculations the β values have been evaluated by the Wolfsberg–Helmholz eqn 1[20]

$$\beta_{AB} = -\beta_0(I_A + I_B)S_{AB} \qquad (1)$$

using benzene calibrated $\beta_0 = 0.435$. Two sets of I_S and A_S values have been applied, besides $I_S = 21.48$ eV and $A_S = 9.44$ eV the values $I_S = 17$ eV and $A_S = 9$ eV were chosen, with $\gamma_{\mu\mu}$ kept constant. The latter small I_S value enabled to scale the critical β_{C-S} and β_{S-S} parameters. Using these values the smallest transition energies of both TTT and NDS were lowered below (slightly) the first experimental excitation energy. However, for TTT the second calculated transition energy was 0.1 eV above the first one with different polarization direction, so this parameter set could not be accepted.

Intermediate values of I_S and A_S turned out to be preferable because the separation of the first two calculated transitions could be increased in this way. In order to have values adaptable to the parametrization scheme given in first column of Table 1, we used the first experimental ionization potential of CH_3SCH_3 (8.67 eV)[21] instead of that of CH_3SH (9.44 eV),[21] corresponding physically to a slightly different valence state of the S atoms involved.

This smaller ionization potential (IP) may be rationalized furthermore by the following argument: even our final set (column 2 Table 1) leads to an IP of TTT (6.01 eV from direct difference of total energies of TTT^+ and TTT; Koopmans theorem leads to 6.11 eV) which is significantly larger than the experimental one (4.56 eV[22] in condensed phase). An increase of the IP of S would cause an even larger discrepancy.

As a next step all β parameters were scaled by changing the value of β_0 in eqn 1, not leading, however, to better results because the modification of the β_{C-C} values has an unfavourable effect.

A better solution proved to be the use of separate β_0 values (2) for C and S atoms in the Wolfsberg–Helmholz equation (A, B are C or S atoms):

$$\beta_{AB} = -(\beta_{0A} + \beta_{0B})S_{AB}(I_A + I_B)/2. \qquad (2)$$

For β_{0C} the original best value for aromatic hydrocarbons was used, for β_{0S} we applied three different smaller values: 0.4, 0.3 and 0.2. The best results were obtained with 0.3. The corresponding parameter set is given in column 2 of Table 1.

RESULTS

The best parameters given in Table 1 give satisfactory agreement with the experimental spectra of NDS and TTT. The corresponding excitation energies, oscillator strengths, and polarization directions of $\pi \to \pi^*$ transitions are given in Table 2.

DISCUSSION

Spectra of NDS and NDT. The second and third calculated transition energies of NDS show very good agreement with the 3.33 and 4.34 eV experimental bands if we suppose that the first calculated energy corresponds to the experimental band system showing three maxima between 2.53 and 2.92 eV. This suggests that the latter three bands correspond to a single weakly allowed $\pi \to \pi^*$ transition, as usually expected for substituted naphtalenes. This is supported by the analogy with the

Table 1. PPP parameters of NDS and TTT calculations (in eV)

	Starting set [18]	Final set
I_C	11.16	11.16
I_S	21.48	20.71
A_C	0.03	0.03
A_S	9.44	8.67
$-\beta_{CC}$	2.39	values around 2.4[a]
$-\beta_{SC}$	1.4	1.91[a]
$-\beta_{SS}$	1.0	1.53[a]

a) According to the modified WH formula (2) with $\beta_{0C} = 0.44$ and $\beta_{0S} = 0.3$. Geometry of TTT is taken from [19], that of NDS and NDT correspond to fragment of TTT. For the calculation of overlap integrals Slater's exponents are used.

Table 2. Spectral data

	Experimental				Calculated		
	E (eV)	f[a]	Pol.dir.	Ref.	E (eV)	f	Pol.dir.
NDS	2.53			[23]			
	2.70	0.01			3.15	0.10	x
	2.92						
	3.33	0.71			3.41	0.43	y
	4.34	0.01			4.25	0.01	x
	4.88	0.38			4.84	0.39	x
					4.94	0.02	y
	5.34	0.14			5.24	0.03	x
					5.35	0.16	y
NDT	3.64	0.06		[24]	3.52	0.13	x
					3.70	0.45	y
					3.74	0.01	x
TTT^{0}	1.77	0.26		[2]	2.28	0.57	y
	1.93	0.17	y b)		2.51	0	
	2.11	0.06					
	2.62	0.19	x b)		2.69	0.51	x
	3.75	sh			3.83	0.13	y
					4.08	0	
					4.25	0	
					4.37	0	
					4.57	0	
	3.97	1.32			4.64	1.41	x
					4.91	0	
	4.96			[28]	5.02	0.01	y
					5.08	0.02	x
TTT^{+}	0.98	0.12		[2,27, 28]	1.45	0.21	x
	0.01	sh					
	1.15	0.07					
	1.32	0.03					
	?1.78 c)	0.02					
	2.14	0.36			2.49	0.49	y
					2.51	0	
	2.31	0.20			2.60	0.01	x
	2.67	0.19			3.12	0.51	x
	3.34	sh			3.22	0	
					3.40	0	
	3.76	0.53			3.84	0.10	y
	4.05	sh					
	4.23	04.8			4.38	0	
					4.60	0	
					4.73	1.04	x
					4.75	0.89	x
TTT^{++}	2.6	strong		[29]	2.89	0.89	x
	2.85	sh			3.17	1.02	y
	3.0	strong					
					3.18	0	
					3.40	0	
					4.39		

(a)The experimental oscillator strengths f are calculated by the formula $f = \epsilon/41{,}700$,[25] ϵ being the molar absorption coefficient in dm^3/mol cm; sh denotes an unresolved shoulder in the experimental spectrum.

(b)This work.

(c)This band is present only in the spectrum of Ref. (2) but not in that of (27). Perhaps it may arise from the first band of TTT^{0} impurities.

pleiadiene spectrum.[23,26] This analogy suggests considerable conjugation interaction through the S–S bond which is reflected in our "best" β_{SS} value. The great similarity[23] of the experimental spectra refer to the strong participation of S atoms in the conjugated system. This effect is also demonstrated by the great change in the spectrum of the corresponding molecule without S–S bond, NDT. The longest wavelength $\pi \to \pi^*$ transition of NDS has much lower energy than that of NDT.

With this assignment the fourth and fifth bands are also in satisfactory agreement with experiment if two transitions are attributed to each band. Intensities agree in the usual quality of the PPP calculations while the polarization directions for both NDS and NDT are experimentally not available.

Spectra of TTT, TTT^+ and TTT^{2+}. We assign the first three bands in the TTT spectrum to one $\pi \rightarrow \pi^*$ electronic transition on the basis of analogy to the spectrum of NDS. The experimental energy difference of the first-second and second-third bands is 1310 cm^{-1} and 1370 cm^{-1}, respectively, being in the order of typical skeletal vibrations. The calculated energy is overestimated by 0.35 eV if we assign the 1.77 eV transition to the $0 \rightarrow 0$ band. The further three bands agree fairly well with the experiment. We emphasize the agreement between the experimental and calculated polarization directions. The trend in oscillator strengths is also well reproduced by the calculation. The first transition of the TTT^+ radical cation is both in theory and experiment much lower than that of TTT, as is natural for radicals. In Table 2 we have tentatively assigned 3 experimental bands to this transition supposing them to the vibrational side bands. The agreement of energies and the intensity ratios are worse, than for the molecules discussed above. The spectrum of TTT^{2+} is in satisfactory agreement with the available experimental data.[29]

The calculated IP is usually overestimated by 1 eV in the PPP method, thus our 6.01 eV value is ~0.5 eV larger than expected. The second IP from our results is 15.48 eV, thus experimental value is expected to be about 14 eV. The disproportionation energy of the reaction

$$2TTT^+ \rightarrow TTT^{2+} + TTT \qquad (3)$$

was calculated to be 3.46 eV, a value in the usual range.[17] As to the charge distribution in TTT and its ions we refer to the experimental ESCA chemical shifts of the S2p core levels.[30] The calculated net π-charges of S are in TTT 0.16, in TTT^+ 0.29 and in TTT^{2+} 0.40. The difference of the first two values is 0.13 which compares with the value of 0.08 obtained from the well-known correlation of chemical shifts and atomic charges.[31] It should be noted that both theory and experiment indicate that only a fraction of the free positive charge is located on the S atoms.

The calculated π-bond orders of TTT and TTT^+ correlate well with observed bond lengths[19,32] as found previously for similar systems.[33] The bond shortening of the S–S and S–C bonds as going from TTT to TTT^+ is of particular interest and can be explained by the fact, that contributions of the highest occupied MO to the corresponding bond orders are negative.

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