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Conformations of the Thiathiophthenes and Related Molecules

Ab initio SCF-MO Calculations

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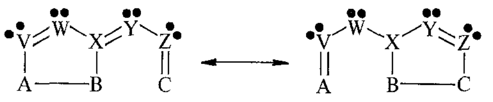
A conformational *ab initio* MO study has been carried out for the thiathiophthene molecule (TTP) and two related model compounds, thiomalonaldehyde (TMA) and its conjugate base (TMA(−)). The conformational energy surfaces for TMA, TMA(−) and TTP were generated using a least squares fit to the calculated data and plotted on a CALCOMP plotter. The results of the calculations showed that the *cis-cis* planar conformation of TTP is the most stable in agreement with experimental findings. For TMA and TMA(−) the *cis-cis* planar conformation is not the most stable. Contour plots of the five occupied π-MO's of TTP show great similarity to those of naphthalene.

Less detailed calculations were carried out for 3-hydroxy-prop-2-en-1-thione (HPT) and 3-mercapto-prop-2-en-1-thione (MPT). HPT was shown to be most stable in the *cis* planar hydrogen bonded conformation in agreement with the experimentally obtained results. For MPT the non-hydrogen bonded planar structure was found to be the most stable.

Key words: Thiathiophthenes, conformations of ∼

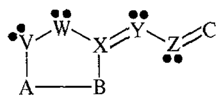
1. Introduction

There is a wealth of crystal structure information showing that the system depicted as (I) ↔ (II) where atoms A, B, C are O, S or Se and atoms V through Z are C or N

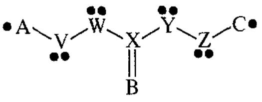


I II

(dots represent either lone or bonding electron pairs) is invariably *cis-cis* planar [1]. The "no-bond resonance" depicted was thought to explain why *cis-trans* (III) or *trans-trans* (IV) conformations are not found even though nuclear-nuclear repulsion would predict the opposite order of stability: (IV) > (III) > (II) = (I). We felt it important to demonstrate by *ab initio* SCF MO calculations that where A, B and C are all sulfur atoms, i.e. in the thiothiophthene (TTP) (V) system, the *cis-cis* conformation is indeed that of lowest energy. Experimentally, the TTP molecule (V) has C_{2v} symmetry and the S–S distances are 2.351 Å [2]. For comparison, an S–S single bond is of the order 2.10 Å to 2.18 Å and the van der Waals diameter is ca. 3.4 Å [3]. All TTP type molecules show aromatic-type UV spectra and when one of the outer hetero atoms is oxygen, the C=O stretching frequency is anomalous [3].



III



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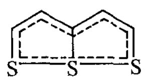
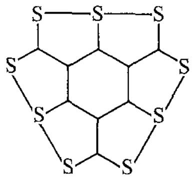


V

The reported synthesis [4] of the TTP analogue of coronene (VI) is further evidence supporting the structural similarity between TTP and naphthalene.



VI

The TTP system has been subjected to considerable theoretical study following the analysis of the crystal structure of the first example, that of 2,5-dimethyl TTP [5].

Hückel MO calculations [6, 7] treating TTP as a naphthalene-like system indicated weak σ- and π-bonding between the sulfur atoms. An eight π-electron treatment has also been considered [8]. PPP-SCF MO calculations [9] utilizing the ten π-electron model for TTP predicted ionization potentials and UV spectra consistent with experimental results. The sigma S–S–S interaction has been compared [10] to the four-electron three-centre bond in I_3^-. CNDO/2 [11, 12] and *ab initio* [13] calculations on symmetrically substituted and unsubstituted TTP agree with experimental evidence [13] supporting a symmetrical structure.

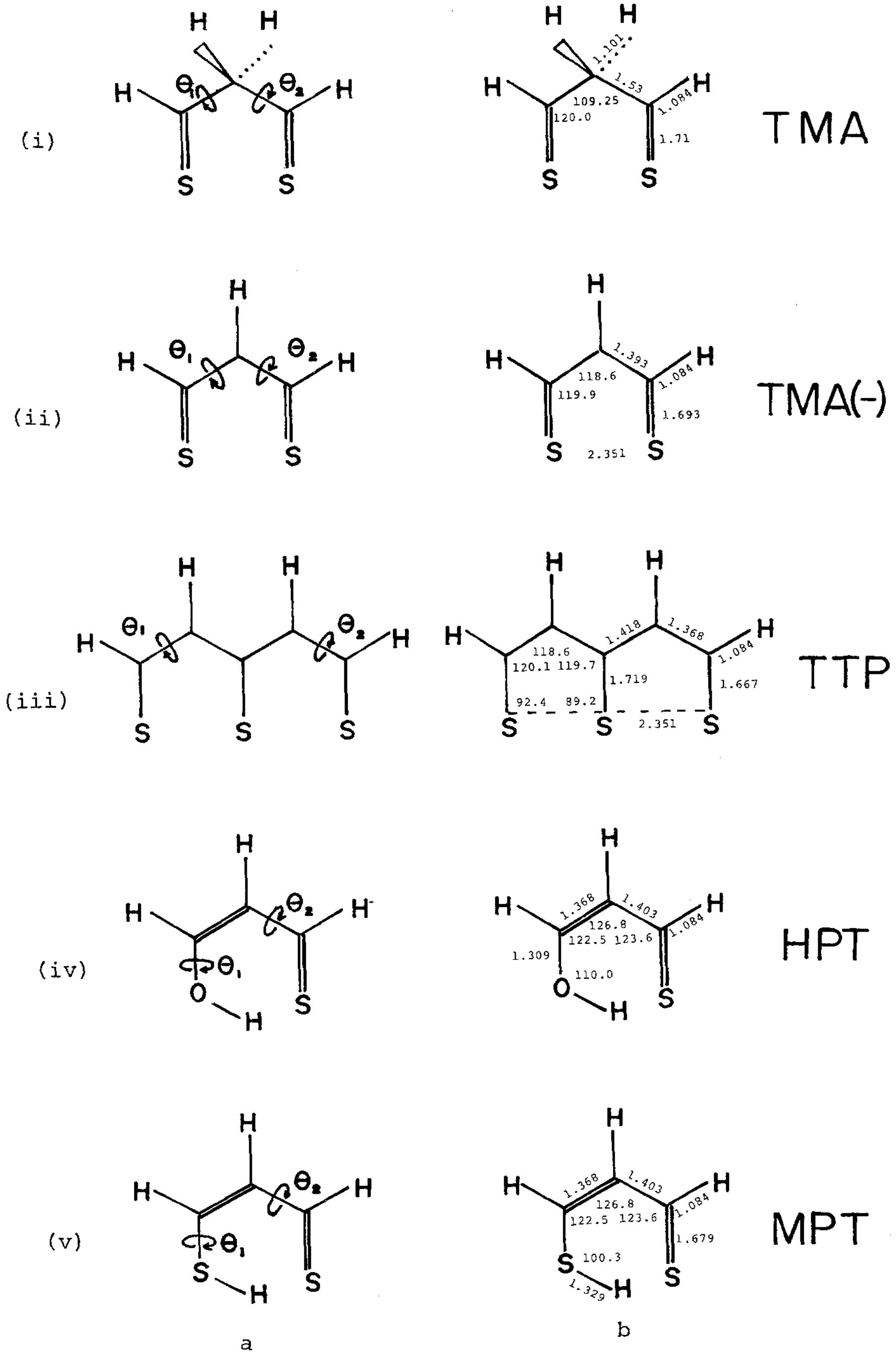


Fig. 1. a) θ_1 and θ_2 angles, b) molecular geometry at (0°, 0°)

The role of sulfur *d*-orbitals in TTP has also been investigated [13]. Apparently these are not necessary to explain the electronic structure of these molecules, a result confirmed in the present work.

As preliminaries to our calculations on TTP, we carried out quite extensive conformational calculations on thiomalonaldehyde (TMA), Fig. 1(i) and its conjugate base (TMA(−)), Fig. 1(ii). Our less extensive calculations on 3-hydroxyl-prop-2-en-1-thione (HPT), Fig. 1(iv), and 3-mercapto-prop-2-en-1-thione (MPT), Fig. 1(v), were prompted by the recent crystal structure analysis of the 1,3-diphenyl derivative of HPT [14].

2. Method of Calculation

Molecular geometries of the compounds studied are given in Fig. 1. For TTP, the experimental geometry [3] is used. The geometry of HPT was obtained from the structure analysis of the diphenyl substituted compound. For TMA, TMA(−) and MPT experimental geometries are not available. For TMA(−) the molecular dimensions were obtained by analogy with those of TTP, while for TMA and MPT they were chosen from published standard bond lengths and angles [15]. The total energy was computed for a range of values of the two angles of rotation θ_1 and θ_2 defined for each structure as in Fig. 1. Note that, in every case, due to symmetry, $E(\theta_1, \theta_2) = E(\theta_2, \theta_1)$.

All calculations were carried out with *s* and *p* Gaussian-type functions (GTF) contracted to a minimal basis set, STO-3G [16], using a version of the GAUSSIAN 70 program [17]. Computational costs for *ab initio* MO calculations on molecules as large as thiathiophthene are very considerable. Consequently, we have been forced to use minimal basis set on enough conformations to generate the conformational hypersurface.

Conformational energy surfaces were expressed in the form of incomplete Fourier series, the coefficients being judiciously chosen for each molecule to give, using the program SURFGEN [18], a least squares fit to the calculated energy values.

3. Results

3.1. *Thiamalonaldehyde* (*TMA*)

The total energies were calculated for 31 different conformations of this molecule. The fitted surface is shown in Fig. 2. Most conformations have comparable energies except those in the immediate neighbourhoood of the *cis*-planar conformation which corresponds to the maximum energy point on this surface. The most stable conformation with total energy of −900.754828 Hartree, is non-planar with the sulfur atoms away from each other, corresponding to the (110°, 250°) point on the surface. These results show that the S–S bonding interaction in the *cis* planar conformation is not important and the nuclear repulsion is predominant.

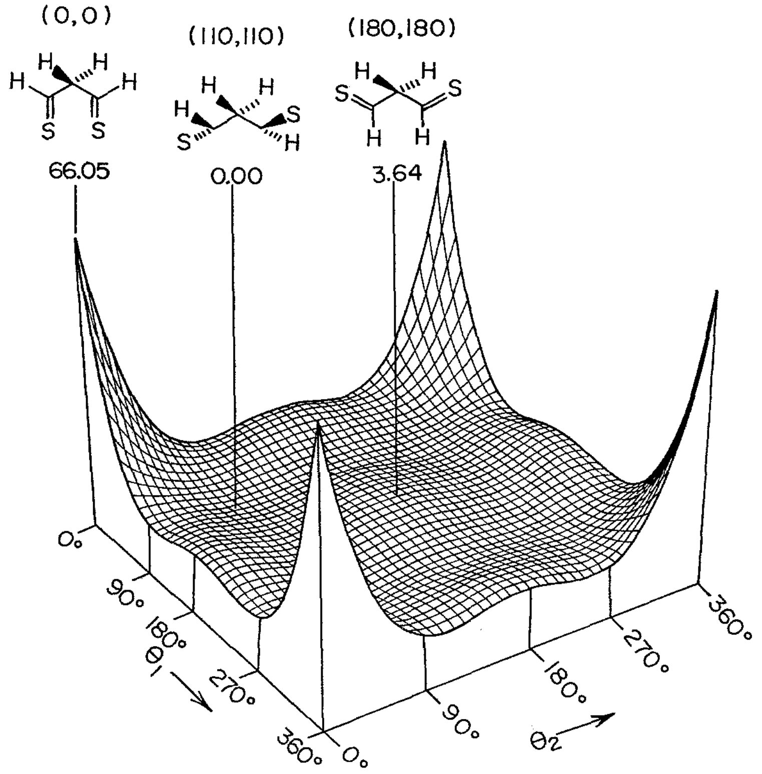


Fig. 2. The conformational energy surface for the TMA molecule

3.2. *Thiomalonaldehyde Ion* (*TMA*(−))

The total energies of 22 conformations of this molecule were calculated. The conformational energy surface is given in Fig. 3. As shown, the most stable conformation with total energy of −900.085197 Hartree, is planar with the two sulfur atoms away from each other, corresponding to point (180°, 180°) on the surface. TMA(−) as shown in VII is a six π-electron system and it is surprising that the planar cyclic structure is not stabilized but it is a maximum energy point on the surface. Further investigation showed that the S–S distance of 2.351 Å, chosen to equal that in the thiathiophthene molecule, is too large for a stabilizing S–S interaction. In fact, the S–S overlap is negative (−0.163 electrons) implying a repulsive S–S interaction. A stable *cis* planar conformation occurs at a S–S distance of 2.11 Å (Fig. 4) which is about the length of a "normal" S–S single bond. At this distance, the S–S overlap is positive, (+0.172 electrons) and the *cis* planar conformation is stable with respect to rotation (Table 1). However, it is still only a local minimum, the (180°, 180°) conformation being the lowest in energy. This result

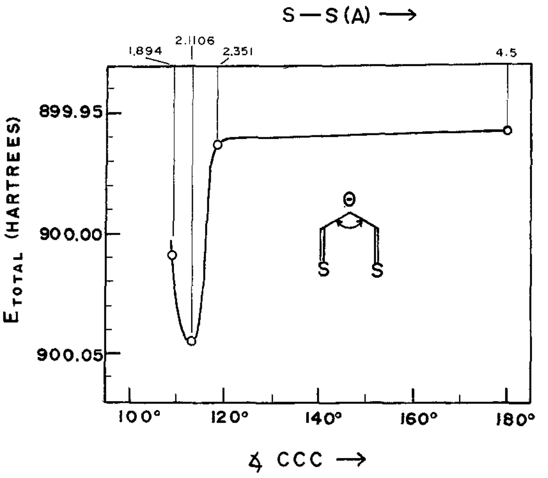


Fig. 3. Total energy of TMA(–) as a function of the CCC angle (and S–S distance)

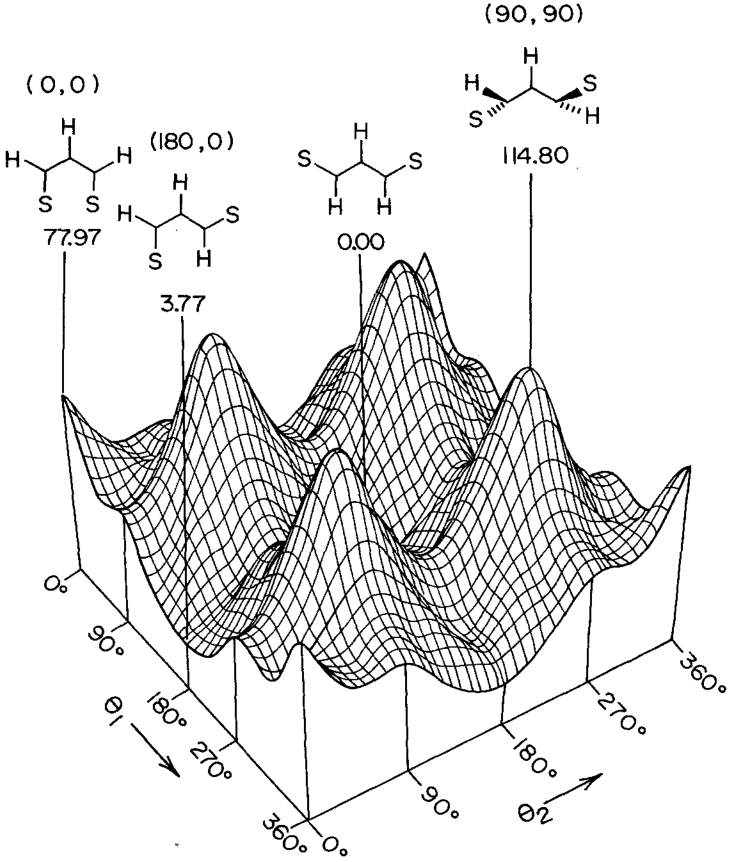


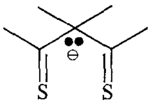
Fig. 4. The conformational energy surface for the TMA(–) ion

Table 1. Total energy of the (0°, 0°) and (180°, 180°) conformations of thiomalonaldehyde anion [TMA(−)]

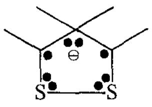
(θ_1, θ_2)	E_{Total} (Hartree)
(180, 180)	−900.085197
(0, 0)[a]	−899.960230
(0, 0)[b]	−900.044986
(0, 15)[b]	−900.039245

[a] S–S = 2.351 Å. [b] S–S = 2.11 Å.

is consistent with the fact that a structure with a formal S–S single bond results in an eight π-electron system (VIII).



VII



VIII

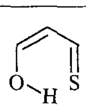
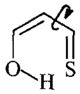
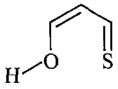
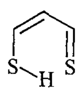
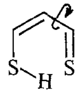
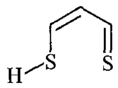
3.3. *3-Hydroxyl-prop-2-en-1-thione* (*HPT*) *and 3-mercapto-prop-2-en-1-thione* (*MPT*)

Crystal structure analysis of 3-hydroxy-1,3-diphenyl-1-prop-2-en-1-thione [14] shows that this molecule is planar. Our calculations on the unsubstituted parent molecule HPT (VIII) and its sulfur analogue (MPT) (IX), were limited to three conformations for each and the results are given in Table 2(a) and (b). It is shown that for HPT the hydrogen bonded structure [first entry in Table 1(a)] is the most stable in agreement with crystallographic results [15]. For MPT the most stable structure was found to be again planar but not hydrogen bonded. It may be noted that the *cis anti*planar conformation of MPT is 0.028646 Hartree lower in energy than the most stable (110°, 50°), TMA conformation. Thiamalonaldehyde would be expected to therefore exist in the "enol" form, or as MPT.

3.4. *Thiathiophthene* (*TTP*)

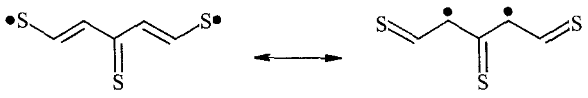
The total energy for 13 conformations of the thiathiophthene molecule was calculated. The fitted surface is shown in Fig. 5. As shown, the *cis-cis* conformation corresponds to the minimum on the surface, and, $E(0°, 0°) = -1368.771484$ Hartree. Conformations having $\theta_1 = 0°$ (or $\theta_2 = 0°$) are low in energy with a local minimum at the (0°, 180°) i.e. *cis-trans* conformation. The barrier to rotation from *cis-cis* to *cis-trans* going through a (0°, 90°) saddle point, is 35.3 kcal/mole (Fig. 6). Elsewhere the energy rises extremely steeply (Fig. 7). No energies were calculated in the region where the smaller θ angle exceeded 45° as the closed shell SCF procedure is inadequate to describe bond-breaking processes.

Table 2. The computed total energy values for 3-hydroxy-prop-2-en-1-thione (a), and 3-mercapto-prop-2-en-1-thione (b)

Conformation		(θ_1, θ_2) Deg.	E_T (Hartree)
(a)		(0, 0)	−581.461790
		(0, 15)	−581.457398
		(180, 0)	−581.439913
(b)		(0, 0)	−900.761758
		(0, 45)	−900.770982
		(180, 0)	−900.783474

Sum of atomic energies: $SC_3H_3OH = -580.395873$
$SC_3H_3SH = -899.721942$

The *trans-trans* conformation of TTP would have to be written as a diradical, (VIIIa, b), thus explaining the very steep rise in energy as the *trans-trans* conformation is approached.



IXa IXb

Net atomic charges (= atomic number minus total electronic charges) are shown in Figs 8a and b for the *cis-cis* (0°, 0°) and *cis-trans* (0°, 180°) conformations. The variation of charge on the sulfur atoms is shown in Fig. 9.

Electron densities for the five π-type MO of TTP are illustrated in Fig. 10 for the *cis-cis* (0°, 0°) conformation on two planes for each MO: one normal to the molecular plane on a line through the sulfur atoms [Fig. 10(i)], the other parallel to the molecular plane and 0.5 Å from it, Fig. 10(ii).

Adjacent to each pair of electron density plots, the symmetry of the corresponding MO for naphthalene is shown [Fig. 10(iii)]. It is seen that π-type bonding in the *cis-cis* conformation of TTP is very similar to that of naphthalene.

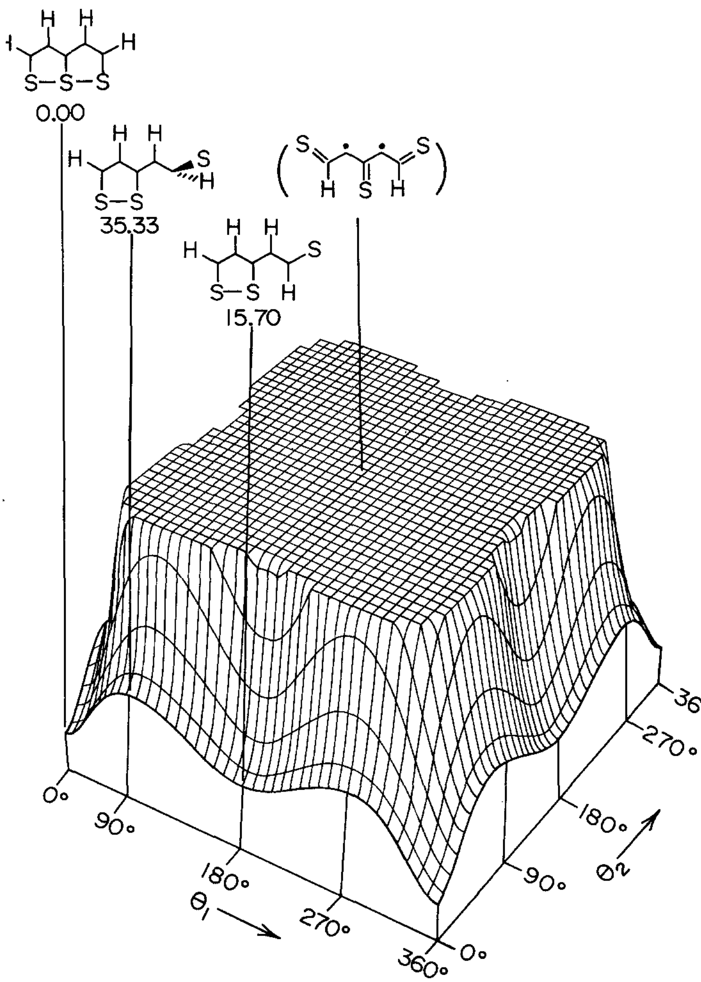


Fig. 5. The conformational energy surface for the TTP molecule

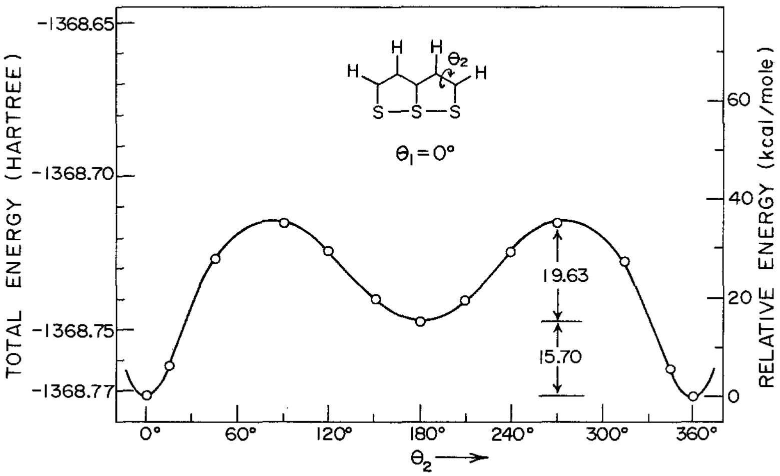


Fig. 6. The energy cross-section for the TTP molecule along $\theta_1 = 0$

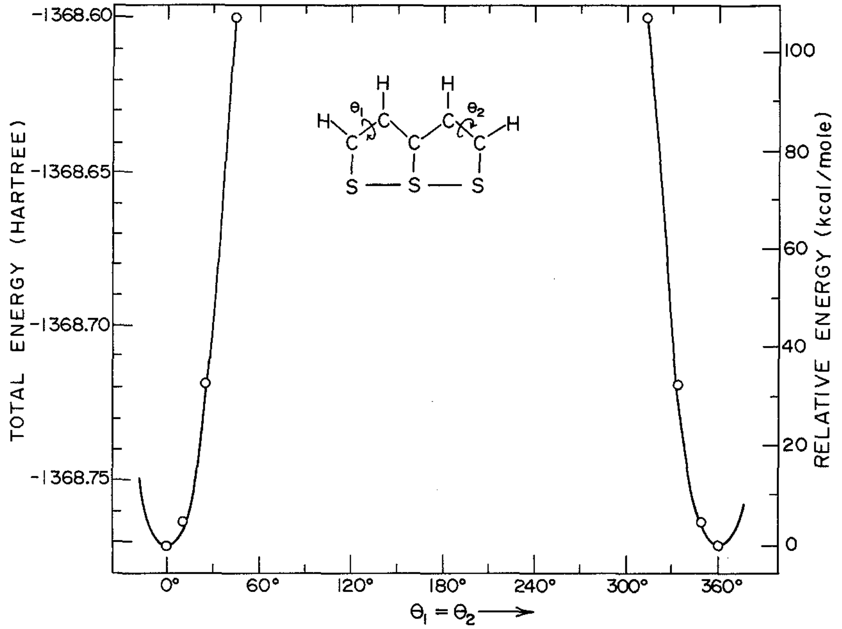


Fig. 7. The energy cross-section along the diagonal ($\theta_1 = \theta_2$) of the conformational energy surface of the TTP molecule

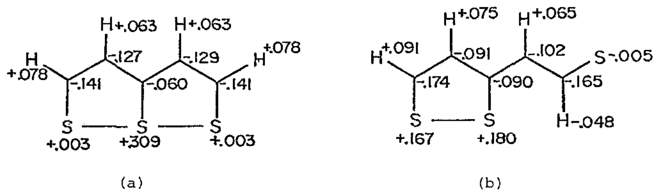


Fig. 8. TTP net atomic charges: a) *cis-cis*, b) *cis-trans*

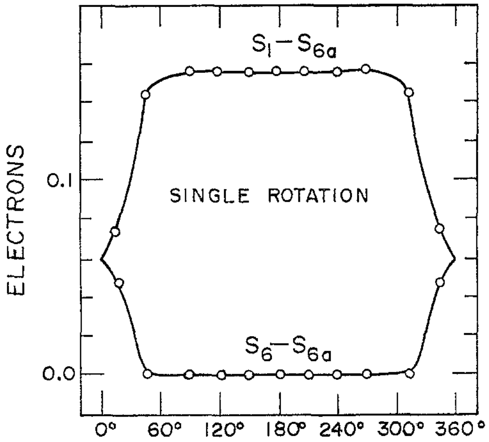
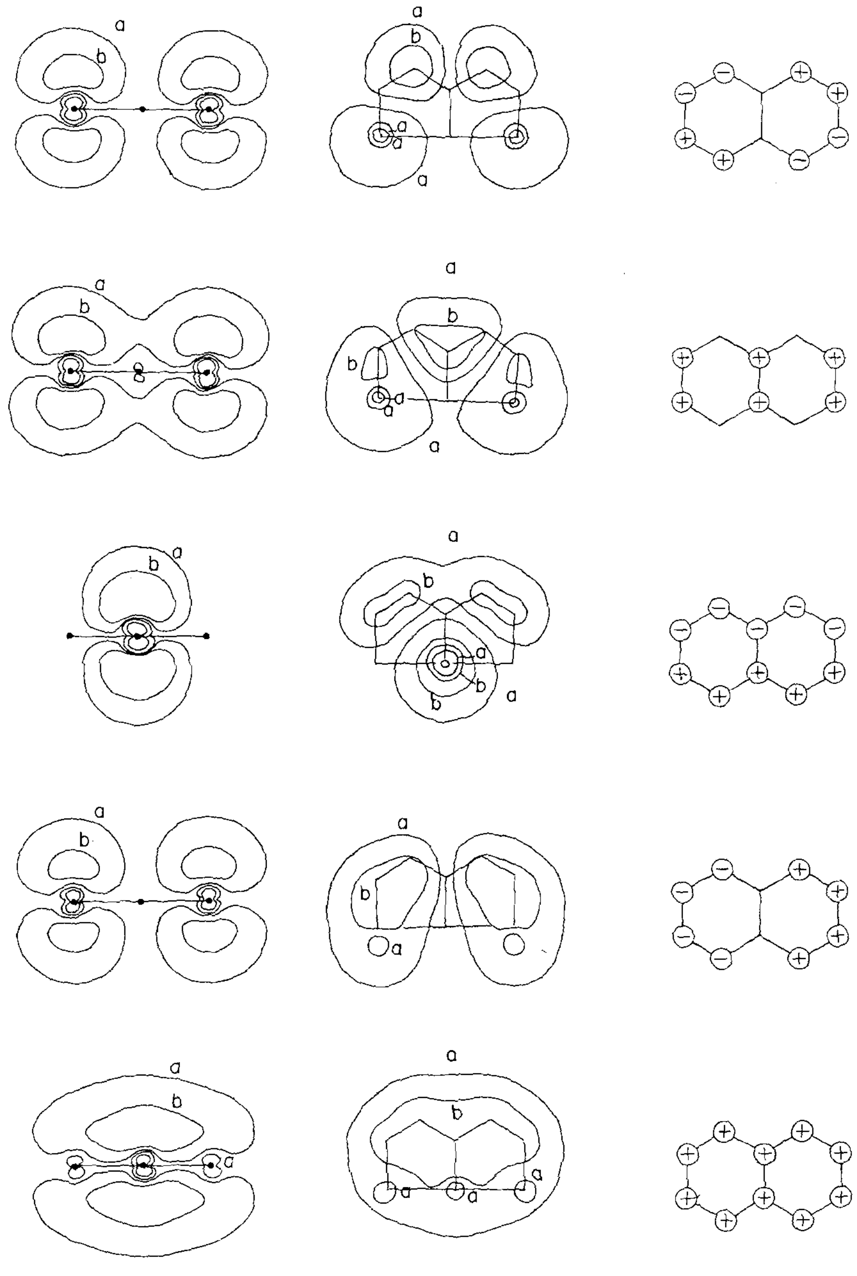


Fig. 9. The variation of electronic charge on the sulfur atoms in TTP with rotation about C_4–C_5



(i) (ii) (iii)

Fig. 10. Contour plots of the electron densities of the five occupied π-type MO of TTP: $a=0.002$ electrons/a_0^3, $b=0.02$ electrons/a_0^3; (i) on a plane perpendicular to the molecular plane and along the S–S–S line, (ii) on a plane parallel to the molecular plane and 0.5 Å above it, (iii) a schematic diagram of the five occupied π-type MO of naphthalene

The results of the calculations on TTP are in full accord with the X-ray structure analyses of this class of compounds, showing that the *cis-cis* conformation is by far the most stable, with an energy barrier of 0.056287 Hartree (35.55 kcal/mole) to the *cis-trans* conformation. This is in interesting contrast with TMA and TMA (−), where the *cis-cis* conformations of these (unknown) molecules are not the most stable structures, indicating that the presence of the third sulfur atom is required in order to stabilize this conformation.

The *cis-cis* conformation, even though the most stable, has the greatest nuclear repulsion energy of all conformations ($E_{n,n} = 573.240744$ Hartree). Clearly it is the substantial delocalized naphthalene-like π-bonding which is stabilizing this conformation as opposed to the *cis-trans* ($E_{n,n} = 530.515614$ Hartree).

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