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The Geometry of Tetrathiotetracene as a Donor in Charge Transfer Complexes: an *ab Initio* Theoretical Investigation

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Ab initio STO-3G calculations are performed on both tetracene (T) and tetrathiotetracene (TTT), and their respective radical-cations. Mulliken populations indices and nodal structure of the HOMO explain the geometry changes of these compounds upon ionization. The strong relaxation energy calculated for tetrathiotetracene, and its low first ionization potential, are related to the grafting of the two disulfide bridges and largely justify the peculiar behavior of TTT upon charge transfer complexation.

INTRODUCTION

In the family of organic electron donors, tetrathiotetracene (TTT) breeds some of the best conducting charge transfer complexes known to date.¹⁻¹³ Reacting TTT with electron acceptors such as *o*-chloranil, *o*-bromanil,¹ TCNE,¹ TCNQ^{3,10} or organometallic molecules,^{11,13} raises its room temperature conductivity ($10^{-4} \Omega^{-1} \text{ cm}^{-1}$ ^{1,2,5-7}) by up to 7 orders of magnitude ($10^3 \Omega^{-1} \text{ cm}^{-1}$ in TTT₂I₃²). By contrast, tetracene (T), having no disulfide bridges, presents a relatively higher oxidation potential and does not form good conducting charge transfer complexes.

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TABLE I

Comparison of the mean molecular TTT dimensions (Å) in various charge transfer complexes. TSeT₂Cl has been added for information

	TTT ¹⁹	TTT ₂ I ₃		TTTBr ²⁵	TTT ₂ ²⁺ Cu ₂ Br ₄ ²⁻²⁶	TTT(TCNQ) ₂ ²⁷	TSeT ₂ Cl ²⁸
		20	24				
S—S	2.100	2.087	2.078	2.075	2.076	2.083	—
S—C ₂	1.781	1.735	1.738	1.744	1.734	1.730	—
C ₁ —C ₂	1.406	1.405	1.390	1.393	1.398	1.40	1.388
C ₂ —C ₃	1.374	1.41	1.414	1.417	1.426	1.435	1.406
C ₃ —C ₇	1.450	1.42	1.411	1.426	1.412	1.425	1.418
C ₇ —C ₈	1.366	1.365	1.359	1.362	1.369	1.36	1.356
C ₁ —C ₆	1.422	1.43	1.430	1.442	1.440	1.38	1.452
C ₃ —C ₄	1.455	1.44	1.444	1.443	1.441	1.41	1.444
C ₈ —C ₉	1.421	1.42	1.405	1.383	1.428	1.40	1.424

Efficient charge transportation in organic donors has often been related to an increase of aromaticity,¹⁴ reflected by modifications of their molecular structure. Indeed, X-ray diffraction measurements on various complexes of TTT reveal significant geometry perturbations of the TTT skeleton with respect to the neutral entity. Table I compares mean molecular dimensions in TTT, TTT₂I₃, TTTBr, TTT²⁺Cu₂Br₄²⁻ and TTT(TCNQ)₂; bond lengths and bond angles conventions are defined in Figure 1. TSeT₂Cl has also been included for illustrative purpose.

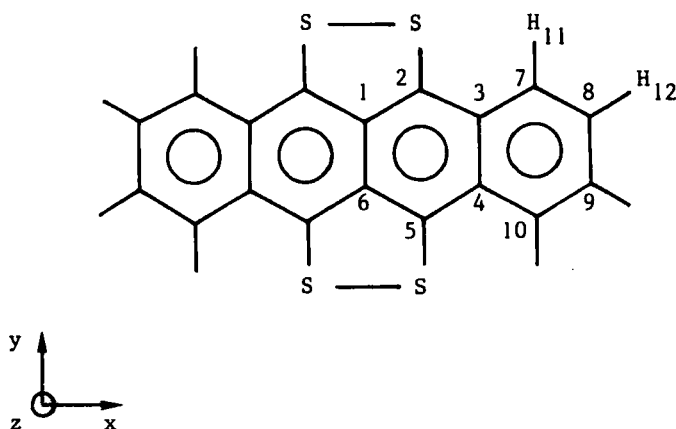


FIGURE 1 Schematic representation of the molecular structure of TTT. The numbering of atoms relates to the contents of Table I and also holds for T.

Theoretical electron density indices (Mulliken charges and overlap populations) can serve not only in establishing the most likely valence bond structures, which provide convenient pictures of the chemical bonding, but also in characterizing aromaticity. Despite the widespread interest in TTT compounds, very little has been done to present a theoretically based interpretation of these geometry changes, besides a short and incidental mention in the work of Kiss *et al.*,¹⁵ mainly devoted to a theoretical assignment of the longest wavelength transition of TTT using the Pariser–Parr–Pople method.

In this communication, we report *ab initio* electronic structure calculations on neutral and cationic radical forms of both T and TTT, to compare their aromaticity pattern and interpret the geometry changes observed in the TTT charge transfer complexes.

COMPUTATIONAL DETAILS

To avoid parametrization difficulties encountered in the work by Kiss *et al.*,¹⁵ it was desirable to apply *ab initio* LCAO–SCF–MO methods. However, the size of the compounds imposed the use of standard minimal STO-3G basis¹⁶ without d orbitals. Fortunately for that class of molecules, the role of 3d atomic functions is reasonably well understood⁷ and consists mainly in a reduction of the polarity of the sulfur containing bonds, without drastically modifying the overall bonding picture as provided by the simple STO-3G basis.

In this preliminary study, calculations were carried out on a limited number of preassigned structures, using the GAUSSIAN 76 program,¹⁷ running on a DEC 2060 computer. All integrals larger than 10^{-6} were explicitly retained and the convergence threshold on the density matrices was always smaller than 5.10^{-5} . Closed shell neutral molecules and radical-cations were respectively treated in the restricted and unrestricted versions of the LCAO–SCF–MO method.

In correspondence with the conventions defined in Figure 1, structural parameters used in the calculations are given in Table II, and D_{2h} symmetry was assumed in all cases. Bond lengths and bond angles for the neutral tetracene and tetrathiotetracene, T and TTT, are taken from experimental results.^{18,19}

Ionized tetracene and tetrathiotetracene, T^+ and TTT^+ , have been calculated in the structure of their neutral parent to catch nascent (or diabatic) changes in electron density indices, thereby hoping to avoid values biased by different geometry readjustments. In the case of TTT, an additional calculation has been made, hereafter denoted by TTT_0^+ ,

TABLE II

Relevant interatomic distances (Å) and angles used in
the calculations on tetracene and tetrathiotetracene

	T	TTT	TTT ⁺ _{relaxed}
S—S	—	2.100	2.078
S—C ₂	—	1.782	1.738
C ₁ —C ₆	1.460	1.422	1.430
C ₁ —C ₂	1.400	1.406	1.391
C ₂ —C ₃	1.390	1.373	1.414
C ₃ —C ₄	1.420	1.456	1.452
C ₃ —C ₇	1.420	1.450	1.411
C ₇ —C ₈	1.380	1.366	1.358
C ₈ —C ₉	1.460	1.422	1.418
S—S—C ₂	—	95.96	95.61
S—C ₂ —C ₁	—	112.59	113.99
C ₂ —C ₁ —C ₆	118.0	118.55	119.61
C ₁ —C ₂ —C ₃	122.84	122.96	121.83
C ₂ —C ₃ —C ₄	119.16	118.49	118.56
C ₄ —C ₃ —C ₇	119.84	117.69	118.31
C ₃ —C ₇ —C ₈	120.32	121.91	121.35
C ₇ —C ₈ —C ₉	119.84	120.40	120.34
C ₂ —H	1.080	—	—
C ₇ —H	1.080	0.860	0.860
C ₈ —H	1.080	0.960	0.960

using the experimentally relaxed geometry of TTT as found in the TTT₂I₃ complex.²⁰

In the case of unrestricted HF calculations, the value of (S^2) is 0.8225, 0.8493 and 0.8586 for T⁺, TTT⁺ and TTT₀⁺ respectively; this is an acceptable discrepancy with respect to the theoretical value of 0.75.

These calculations on the neutral and ionic forms of the donors are evidently meant to measure only the direction of change in structure upon complex formation especially because no geometry optimization has been carried out.

DISCUSSION

Table III collects total energies, electronic charges and π -overlap populations for the five systems: T, T⁺, TTT, TTT⁺ and TTT₀⁺. In the case of neutral forms, we have added the energy of the highest occupied molecular orbital (HOMO) and its irreducible representation label. A schematic representation of the nodal structure and the

TABLE III

Theoretical results on T, T⁺, TTT, TTT⁺, TTT₀⁺. Total energies in *a.u.* and ϵ_{HOMO} in eV.

	T	T ⁺	TTT	TTT ⁺	TTT ₀ ⁺
Total energy:	-680.23724	-680.11135	-2250.37517	-2250.25961	-2250.30391
ϵ_{HOMO}	-4.41(<i>a_{Iu}</i>)	—	-3.66(<i>a_{Iu}</i>)	—	—
Electronic charges:					
S	—	—	15.890	15.786	15.773
C ₁	6.003	6.011	6.013	6.018	6.020
C ₂	6.060	5.995	6.098	6.062	6.070
C ₃	6.002	5.982	5.993	5.971	5.970
C ₇	6.061	6.042	6.124	6.112	6.113
C ₈	6.062	6.024	6.071	6.041	6.042
π -overlap populations:					
S3 <i>p_z</i> —S3 <i>p_z</i>	—	—	-0.008	0.000	0.001
S3 <i>p_z</i> —C2 <i>p_z</i>	—	—	0.016	0.030	0.035
C2 <i>p_z</i> —C2 <i>p_z</i> :					
C ₁ —C ₂	0.089	0.091	0.083	0.086	0.093
C ₂ —C ₃	0.111	0.086	0.116	0.093	0.077
C ₃ —C ₇	0.060	0.075	0.054	0.066	0.079
C ₇ —C ₈	0.147	0.131	0.151	0.141	0.136
C ₁ —C ₆	0.069	0.048	0.075	0.065	0.053
C ₃ —C ₄	0.069	0.074	0.064	0.074	0.077
C ₈ —C ₉	0.059	0.073	0.061	0.071	0.079

participation of *p_z* atomic functions in the HOMO, which has a strict π character, is also given in Figure 2. Other quantities (σ contributions to the total overlap populations, innermost one-electron energy eigenvalues...) have not been reproduced here, since they are either identical in both neutral and charged molecules or irrelevant for our present purposes.

Total energies, which are only indicative values, are distributed on the energy scale as expected: (i) neutral forms, T and TTT, are respectively lower in energy than the charged ones, T⁺ and TTT⁺, TTT₀⁺; (ii) a significant relaxation energy (27.8 Kcal/mole) is calculated between TTT₀⁺ and TTT⁺.

Calculated atomic populations for tetrathiotetracene indicate that, upon electron withdrawal, sulfur atoms and, to a lesser extent, adjacent carbons support the main part of the electron deficit, while other carbons are only slightly affected by the ionization process. Going from the neutral TTT to the relaxed geometry does not affect the picture, the charges being almost identical in both cases. The changes in populations going from TTT₀⁺ to TTT⁺ are very similar to the changes in T to T⁺, and therefore constitute a poor measure by which

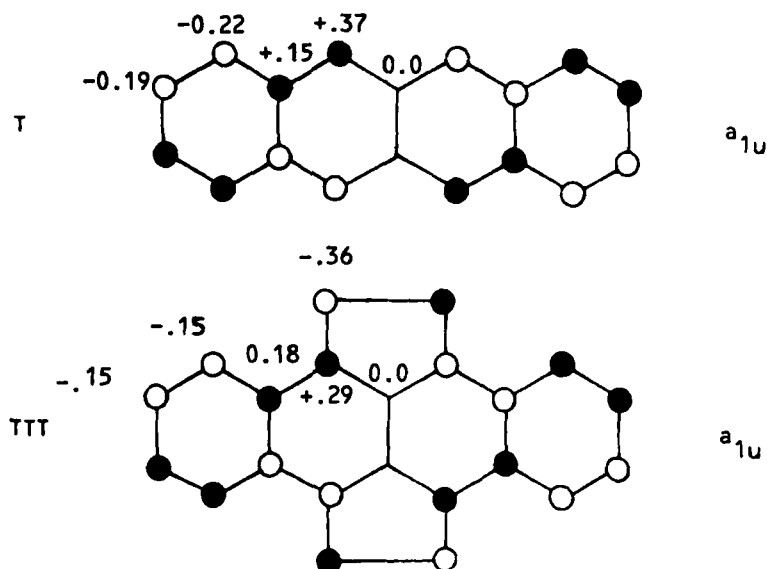


FIGURE 2 Schematic representation of the nodal structure of the HOMO in T and TTT.

to discriminate between the different behaviors of the two systems upon charge transfer complexation.

The π -overlap populations, contrary to the σ contributions, are more sensitive to the ionization. Already in the frozen geometry of their neutral forms, π -overlap populations of T^+ and TTT^+ molecules readjust significantly and are indicative of the geometry evolution. In both cases, the tendency is towards a slight shortening of C—C bonds together with an increase of C=C bond lengths.

This tendency could have been anticipated on the basis of the nodal structure given in Figure 2. A partial depopulation of the HOMO in tetracene and tetrathiotetracene induces lengthening (shortening) in bonding (antibonding) regions. A closer inspection of the π -overlap populations reveals the following points:

—In tetrathiotetracene, the departure of one electron leads to a shortening of the S—S bonds, probably due to a reduction in the electron density on the sulfur lone pairs, and a corresponding decrease in the electron repulsion.⁷ The five-membered rings shrink and the $S3p_z$ — $C2p_z$ overlap populations become twice as large. These predicted trends of bond length evolution are confirmed by experimental data^{20,24–27} and support the involvement at the sulfur lone pairs in the

conjugated system.^{7,15} That is, with the peculiar stacking mode and the low interplane spacings between radical-cations, a further indication of the active participation of the sulfur lone pairs in the charge transport.

Ionization has comparable effects on the four-ring system both tetracene and tetrathiotetracene. The larger $C2p_z-C2p_z$ overlap populations (C_1-C_6 , C_2-C_3 , C_7-C_8) are weakened in the ionic forms, while the reverse occurs for the smaller ones (C_1-C_2 , C_3-C_4 , C_3-C_7 , C_8-C_9).

These calculated trends are all confirmed by experiment, except for the C_7-C_8 bond for which X-ray data show a shortening instead of an increase of the bond length. This discrepancy is to be related to the unusually short interatomic contacts, observed in TTT_2I_3 and $TTTBr$, between the halogen(s) and the C_7 , C_8 , H_{11} and H_{12} atoms of TTT. Such a situation does not occur in neutral TTT and has not been accounted for in our calculations on the cations.

If theoretical charge indices in this preliminary study agree well with experiment on the structural changes observed in tetrathiotetracene complexes, they also leave open questions about the aromatic character of TTT^+ compared to T^+ . From Table III, we observe that the same qualitative trend occurs for both systems. Overlap populations, here the π ones, which have met with considerable success in establishing valence bond structures, are fully qualified to search for the existence of specific aromatic character in TTT^+ compared to T^+ . Such a distinctive feature has not been found here: thus, our results do not support the suggestion that donors and acceptors having high electrical conductivity form a new aromatic sextet.¹⁴

However, some differences between tetracene and tetrathiotetracene, that are relevant to their electronic behaviour, can be explained theoretically at the molecular level. First, assuming the validity of Koopman's theorem, we can relate the HOMO energies of T and TTT to their ionization potentials. Calculations show a strong destabilization of the T-HOMO when two disulfide bridges are grafted to form TTT. This has been experimentally observed by X.P.S., which gives values of 1.5 eV and 0.9 eV for the first ionization potentials of tetracene and tetrathiotetracene respectively⁷, and is related to the antibonding nature of the mixing occurring between $S3p_z$ and $C2p_z$ atomic functions (Figure 2).

Secondly, on the basis of the rough stabilization energy (27.8 Kcal/mole; STO-3G basis) obtained in going from TTT^+ to TTT_0^+ , we anticipate strong differences in the way tetracene and tetrathio-

tetracene accommodate the electron deficit created by ionization. Indeed, the same calculation for T_0^+ —using the geometry of TTT_0^+ —leads to higher total energy compared to T^+ , suggesting that the experimentally relaxed geometry of TTT_0^+ is too much rearranged for T_0^+ .

These two points explain the different ability of T and TTT to act as good electron donors.

CONCLUSIONS

The molecular structure evolution of tetrathiotetracene from neutral species to radical-cation is well interpreted in terms of Mulliken indices and nodal structure of the HOMO. In both T^+ and TTT^+ , the C—C bond pattern rearranges so as to spread the perturbation over the whole molecule. However, Mulliken population analysis does not allow to discriminate T^+ and TTT^+ from the viewpoint of the stabilization of the positive charge. These question should be considered on a more quantitative basis and extensive geometry optimizations should be made to obtain a more consistent picture of the relative stability of these radical-cations.

References

1. Y. Matsunaga, *J. Chem. Phys.*, **42**, 2248 (1965).
2. E. A. Perez-Albuern, H. Johnson Jr. and D. J. Trevoy, *J. Chem. Phys.*, **55**, 1547 (1971).
3. L. I. Buravov, O. N. Eremenko, R. B. Lubovskii, L. P. Rozenberg, M. L. Khidekel, R. P. Shibaeva, I. F. Shchegolev and E. B. Yagubskii, *J. E.T.P. Lett.*, **20**, 208 (1974).
4. L. I. Buravov, O. N. Eremenko, R. B. Lubovskii, L. P. Rozenberg, M. L. Khidekel, R. P. Shibaeva, I. F. Shchegolev and E. B. Yagubskii, *J.C.S. Chem. Comm.*, 720 (1976).
5. H. Inokuchi, M. Kochi and Y. Harada, *Bull. Chem. Soc. Jap.*, **40**, 2695 (1967).
6. E. A. Goodings, D. A. Mitchard and G. Owen, *J.C.S. Perkin I*, **11**, 1310 (1972).
7. J. Riga, J. J. Verbist, F. Wudl and A. Kruger, *J. Chem. Phys.*, **69**, 3221 (1978).
8. R. B. Somoano, S. P. S. Yen, V. Hadek, S. K. Khanna, M. Novotny, T. Datta, A. M. Hermann and J. A. Woollam, *Phys. Rev.*, **B17**, 2853 (1978).
9. T. Inabe and Y. Matsunaga, *Bull. Chem. Soc. Jap.*, **51**, 2813 (1978).
10. J. H. Perlstein, J. P. Ferraris, V. V. Walatka, D. O. Cowan and G. A. Candela, AIP Conference Proceedings 3, 1494, Denver (Colorado), (1972).
11. L. V. Interrante, J. W. Bray, H. R. Hart Jr., J. S. Kasper and P. A. Piacente, *J. Am. Chem. Soc.*, **99**, 3523 (1977).
12. J. W. Bray, H. R. Hart Jr., L. V. Interrante, I. S. Jacobs, J. S. Kasper and P. A. Piacente, *Phys. Rev.*, **B16**, 1359 (1977).
13. W. E. Geiger Jr., *J. Phys. Chem.*, **77**, 1862 (1973).
14. J. H. Perlstein, *Angew. Chem. Int. Ed. Engl.*, **16**, 519 (1977).

15. A. I. Kiss, M. Kertesz, P. Carsky and H. Wedel, *Tetrahedron*, **35**, 515 (1979).
16. (a) W. J. Hehre, R. Ditchfield, R. F. Stewart and J. A. Pople, *J. Chem. Phys.*, **52**, 2769 (1970). (b) J. B. Collins, P. v. R. Schleyer, J. S. Binkley and J. A. Pople, *J. Chem. Phys.*, **64**, 5142 (1976).
17. J. A. Pople, J. S. Binkley, R. A. Whitehead, P. C. Hariharan and R. Seeger, *QCPE*, **10**, 368 (1978).
18. R. B. Campbell, J. M. Robertson and J. Trotter, *Acta Cryst.*, **15**, 289 (1962).
19. O. Dideberg and J. Toussaint, *Acta Cryst.*, **B30**, 2481 (1974).
20. D. L. Smith and H. R. Luss, *Acta Cryst.*, **B33**, 1744 (1977).
21. M. G. Kaplunov, Y. M. Shulga, K. I. Poscognya, O. N. Eremenko, E. V. Yagubskii, M. L. Khidekel and Y. G. Borodko, *Teor. Eksp. Khim.*, **11**, 797 (1975).
22. J. P. Boutique, J. Riga, J. J. Verbist, K. Kamaras, A. Janossy and G. Grüner, *Chemica Scripta*, **17**, 57 (1981).
23. J. P. Boutique, PhD. Thesis, Namur (1982), Belgium.
24. R. P. Shibaeva and V. F. Kaminskii, *Sov. Phys. Cryst.*, **23**, 277 (1978).
25. R. P. Shibaeva, V. F. Kaminskii, O. N. Eremenko, E. B. Yagubskii and M. L. Khidekel, *Sov. Phys. Cryst.*, **25**, 31 (1980); *Krystallografiya*, **25**, 60 (1980).
26. R. P. Shibaeva and V. F. Kaminskii, *Krystallografiya*, **26**, 332 (1981).
27. R. P. Shibaeva and L. P. Rozenberg, *Sov. Phys. Cryst.*, **20**, 581 (1976).
28. R. P. Shibaeva and V. F. Kaminskii, *Sov. Phys. Cryst.*, **23**, 1183 (1978).