Charge Density Studies of Thiathiophthene. 4[+] Theoretical Studies on 2,5-Dimethyl Thiathiophthene and 2,4-Diphenyl Thiathiophthene with Density Functional Method

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The distribution of deformation density of 2,5-dimethyl thiathiophthene and 2,4-diphenyl thiathiophthene are calculated via density functional method. The results are in good agreement with the corresponding experimental and theoretical distributions from an ab initio method. The ionization potentials obtained in this calculation on 2,5-dimethyl thiathiophthene are in good agreement with those obtained experimentally from photoelectron spectroscopy, it is in better agreement than those VIPs based on ab initio calculations. Net atomic charges are compared with the experimental multipole refinement and with those calculated with ab initio and DFT methods for various atomic partitions.

INTRODUCTION

The distribution of deformation density has been investigated by X-ray diffraction for some years,[1-5] and multipole model deformation densities[6] are commonly used to compare with those calculated from the ab initio HFSCF method.[7-8] Density functional theory (DFT)[9] is recently considered to be one of the most efficient methods to describe any density-related properties. We believe there is a need to assess the merit of the electron density distribution according to the DFT method.

Orbital energies calculated from HFSCF are commonly used to interpret photoelectron spectra based on Koopmans' theorem.[10] Vertical ionization potentials (VIPs) derived from DFT may agree better with experimental data than those from HFSCF because energy terms might be affected by electronic correlation more than the density distribution.

Two compounds 2,5-dimethyl thiathiophthene(2,5-DMTTP) and 2,4-diphenyl thiathiophthene(2,4-DPTTP) are chosen for such studies using DFT method as their density distributions are thoroughly investigated by low-temperature X-ray diffraction experiments[11-12] and ab initio calculations.[13] The photoelectron spectrum of 2,5-dimethyl thiathiophthene is also known.[14] Both thiathiophthene molecules are planar with two fused five-membered rings.[11-12] The special type of bonding is discussed in terms of an 8-centered 10π-electron aromatic π system and a three-centered four-electron S-S-S σ system.[13] Comparison can be made for the deformation density and VIPs between experimental results[14] and values from ab initio HFSCF[13] and DFT calculation.

COMPUTATION PROCEDURE

There are a few programs available for DFT methods. The ones we used in this work were DMol[15] and deMon.[16-17] The former one uses numerical basis functions, whereas the latter one uses gaussian basis functions. Atomic natural orbitals (ANOs)[18] are used in deMon program and double numerical basis set plus polarization (DNP) is used in DMol program. A basis set of [431; 321; 210] ANOs is used in the calculation with deMon program, where [431], [321] and [210] are basis functions for sulfur, carbon and hydrogen atom, respectively. The notation [IJK] means that there are I, J and K s-, p- and d-type ANOs on each atom. The numerical fitting grid is chosen to be fine and nonrandom; the auxiliary fitting functions are (5,4; 5,4) for sulfur atom, (4,4; 4,4) for carbon atom and (3,1; 3,1) for hydrogen atom. The (k,l; m,n) notation means there are k s-type GTOs plus l sets of s-, p-, d-type GTOs, each set with the same exponent for the charge density fit. The indices m and n represent sizes of similar types for the exchange-correlation fit. The ANOs basis set used here is nearly equivalent to Gaussian 6-31G**. A local density approximation (LDA) is im-

Dedicated to Professor Sung-Mao Wang (王松茂) on the occasion of his seventieth birthday.
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posed with the local V_{xc} of Vosko et al.[19]

In order to calculate VIPs *in* DFT calculations (deMon and DMol), we make a simple approximation to Slater's transition state concept,[20] following Åsbrink et al.[21] Instead of removing half of an electron from the MO of interest, we remove half of an electron evenly from the top ten valence MOs.[22]

The molecular geometry is taken from the low temperature X-ray diffraction measurement.[11-12] The deformation density $\Delta\rho_{DFT}$ is calculated by subtracting the spherical atomic electron density from the molecular electron density as described elsewhere.[7-8] Earlier results of $\Delta\rho_{m\text{-}a}$ and $\Delta\rho_{3\text{-}21G^*}$ are taken from the literature.[13] The DFT calculations are made on IBM DEC5000 and on RISC6000 work stations with deMon and DMol programs, respectively.

RESULTS AND DISCUSSIONS

The distributions of deformation densities of 2,5-DMTTP and 2,4-DPTTP molecules are shown in Fig. 1 and 2, respectively. There are two planes in each figure. The deformation densities of the thiathiophthene (TTP) ring plane is shown in (a, b, c), whereas the plane perpendicular to the TTP plane and through S-S-S is shown in (d, e, f). There are three maps on each plane, the top ones (a, d) are the static multipole model deformation densities from the earlier work;[13] the middle ones (b, e) are the theoretical deformation densities calculated by ab initio molecular orbital calculation[13] and the bottom ones (c, f) are the theoretical ones calculated by DFT method. As maps of deformation density calculated with deMon and DMol programs are essentially

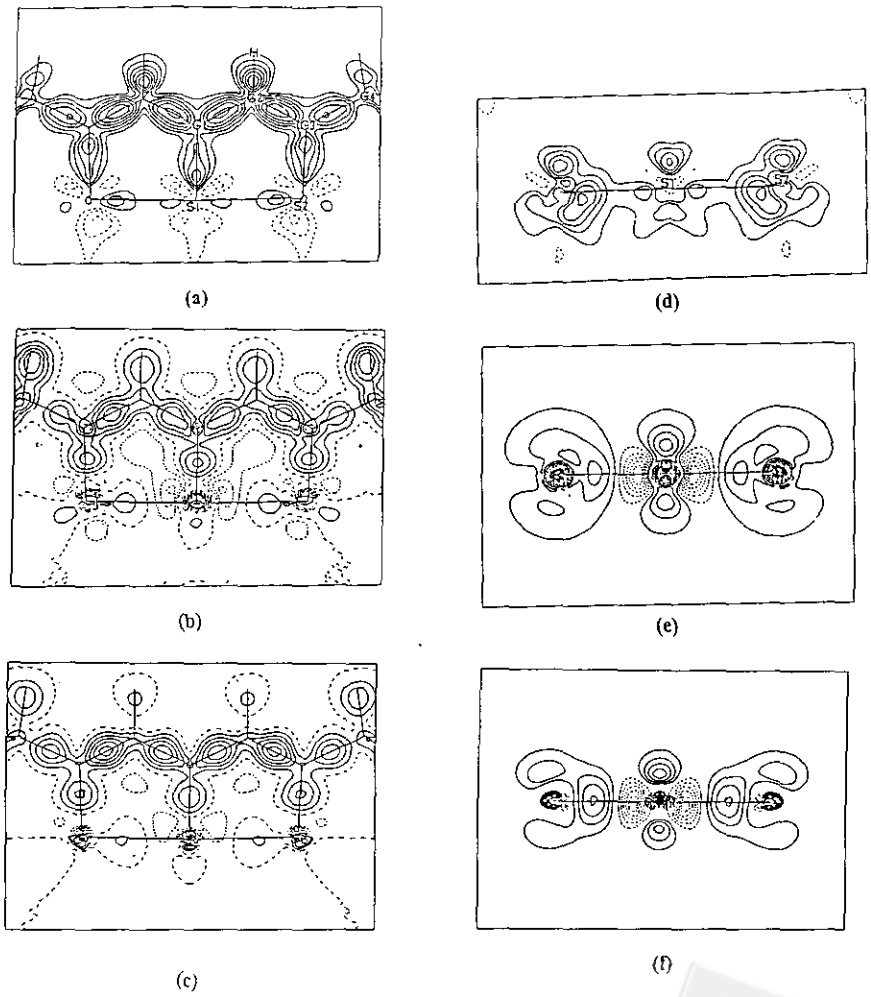

Fig. 1. The distribution of deformation density of 2,5-DMTTP; (a), (b) and (c) are on the TTP plane; (d), (e) and (f) are on the plane perpendicular to TTP plane through the S-S-S region; solid line positive, dashed lin zero, dotted line negative. (a) $\Delta\rho_{M\text{-}A,static}$, contours interval 0.1e Å^{-3}. (b) $\Delta\rho_{3\text{-}21G^*}$, contours as in (a). (c) $\Delta\rho_{deMon}$, contours as in (a). (d) $\Delta\rho_{M\text{-}A,static}$; contours interval 0.05 eÅ^{-3}. (e) $\Delta\rho_{3\text{-}21G^*}$; contours as in (d). (f) $\Delta\rho_{deMon}$; contours interval 0.025 eÅ^{-3}. (a), (b), (d) and (e) are from ref. 13.

the same, the maps presented here for 2,5-DMTTP are calculated with deMon and those for 2,4-DPTTP are results with DMol. It is apparent that the three maps of deformation density (a, b, c) of the TTP plane in both compounds (Fig. 1 and 2) all agree satisfactorily with one another. Perhaps maps from DFT calculations c) agree slightly better with the experimental ones a) than those from ab initio calculation b). However the agreement between maps for the other plane (d, e, f) is not as good as those (a, b, c) of the TTP plane, although features in these three maps are quite similar: the one from DFT (Fig. 1f, Fig. 2f) gives only about half the density; i.e., there is only little density at the plane perpendicular to the TTP ring, so the disagreement signifies little. As the density on this plane (d, e, f) is contributed mainly from the sulfur lone pair electrons, it is apparent that there are not much density on the lone pairs of sulfur atoms at this plane. An alternative way of expressing the charge distribution uses the net atomic charges of the molecule. These charges of the two molecules are presented in Fig. 3, in which different values on each atom arise from various methods and analyses. The top value is obtained from the multipole refinement,[6] the second one from the top from Mulliken population analysis (MPA) out of 3-21G* ab initio MO calculation,[13] and the bottom three values are from DFT method with two programs. There are two values (3rd and 4th) derived from the DMol calculation, one from MPA and the other by means of the Hirshfeld partition;[23] the fifth value is derived from deMon using MPA. The definitions of four values on each atom in b) are the same as the first four values in a). In general, the agreement on atomic charges of sulfur atoms between experimental ones and the ones from DFT are very good based on the experimental error, in con-

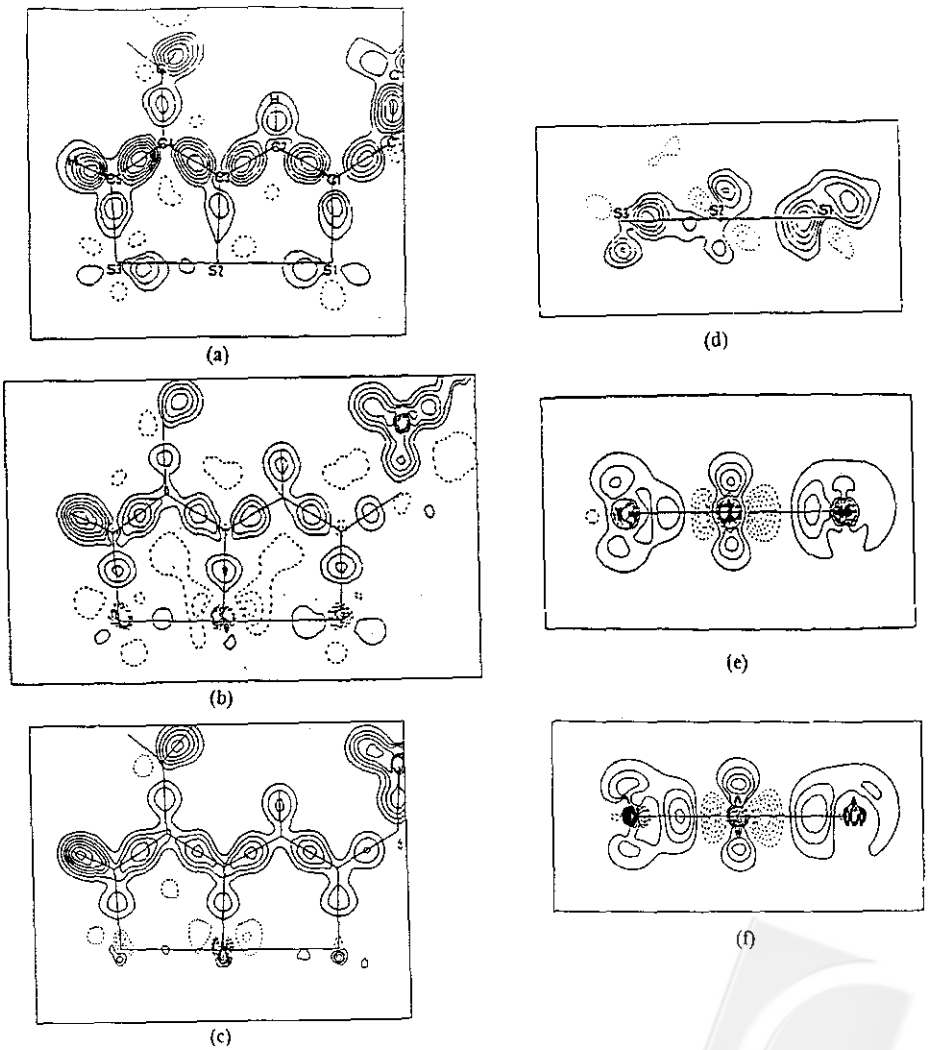

Fig. 2. The distribution of deformation density of 2,4-DPTTP, definitions of (a), (b), (c), (d), (e), (f) and contours correspond to those in Fig. 1a, 1b, 1d and 1e from ref. 13.

trast with values from ab initio calculations with MPA. It is known that charges obtained this way depend strongly on the size of the basis set, and there are severe limitations on values obtained from MPA.[24-26] However, the agreement on carbon and hydrogen atoms is better from ab initio than from DFT. The inconsistences among the values from seperate partitions or basis functions indicate the limitation.

As we discuss the density distribution of these two molecules at their ground states, we compare VIPs from DFT, ab initio MO[13] and from photoelectron spectroscopy[14] in the case of 2,5-DMTTP. The values are given in Tables 1 and 2 for 2,5-DMTTP and 2,4-DPTTP, respectively. The agreement between DFT and experimental ones for 2,5-DMTTP is excellent. However, it is unfair to compare values from DFT with those from ab initio calculations, because the value from ab initio calculation is simply the negative value of the orbital energy, whereas the value from DFT is the energy difference between the transition and ground state. The latter should produce values much closer to experimental ones. Linear relationship between the experimental values (VIP_{obs}) and the calculated ones (VIP_{calc}) exists for both values from DFT (□) and values from ab initio calculations (♦) as shown in Fig. 4. As expected, the slope of the line (1.01) from DFT is close to 1, but 1.57 from ab initio calculation. The slope much greater than one is probably due to the limited basis function and lack of electron correlation in the ab initio calculation. The intercept of the line is -0.14 for DFT and is -4.23 for ab initio calculation. Although ten VIP_{calc} values are listed on the table, only six values are plotted in Fig. 4. The corresponding orbital characters are also assigned according to MO wavefunctions. As there is no experimental values available for 2,4-DPTTP, only calculated VIPs are listed in Table 2 with assigned orbital characters. It is noticeable that the differences of VIP

Table 1. First Ten VIP Values (eV) for 2,5-DMTTP

HFSCF[#] 3-21G*	DFT deMon	DFT DMol	Expt.[§]	Orbital Character
7.97	7.66	7.86	7.73	21a″ $\pi_{C2\text{-}C3,S2}$
8.22	7.90	8.11	7.90	28a′ $\sigma_{S\text{-}S\text{-}S}$
9.90	8.84	9.02	9.08	27a′ $\pi_{S1\text{-}C1}$ $\pi_{S2\text{-}C3}$
10.57	9.15	9.33	9.53	26a′ $\pi_{C\text{-}C\text{-}C}$, $\pi_{S\text{-}S\text{-}S}$
12.03	10.13	10.33	10.04	20a″ $\pi_{C2\text{-}C3\text{-}S2}$
12.43	10.56	10.76	10.70	19a″ $\sigma_{S\text{-}S\text{-}S}$
13.51	11.14	11.33		25a′ η_{S1},η_{S2}
14.25	11.53	11.73		18a″ $\sigma_{C\text{-}C}$, $\sigma_{C\text{-}H(methyl)}$
14.41	11.66	11.84		24a′ $\sigma_{S1\text{-}C1}$, $\sigma_{C2\text{-}H2}$
14.58	11.79	11.98		23a′ π_{ring}

[#] ref. 13
[§] ref. 14

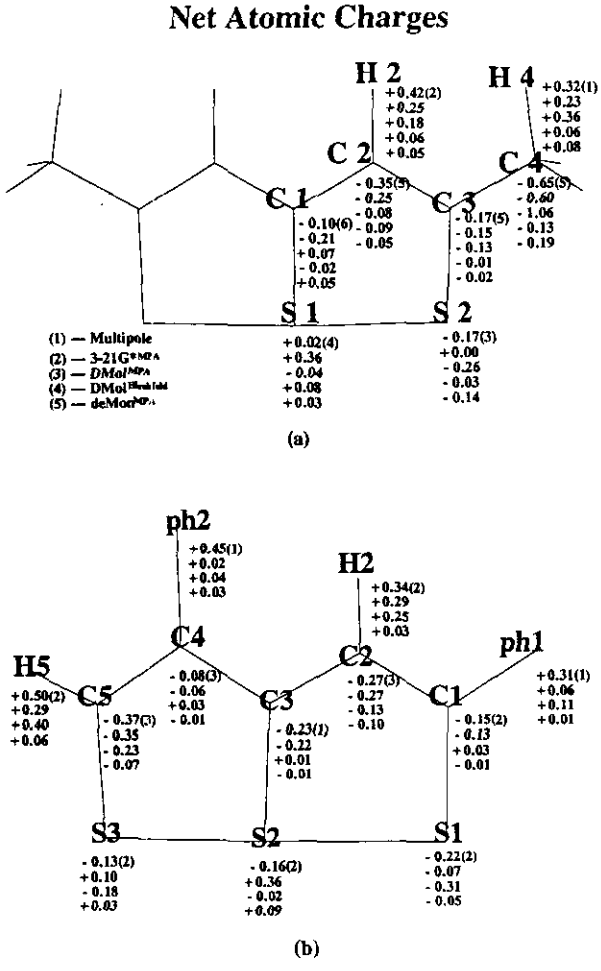

Fig. 3. Net atomic charges for (a) 2,5-DMTTP; five values are given for each atom-top, multipole refinement (ref. 6); second, ab initio with MPA (ref. 13); third, DMol with MPA; fourth, DMol with Hirshfeld partition; bottom, deMon with MPA. (b) 2,4-DPTTP: four values are given for each atom, defined as for the top four values in (a).

Table 2. First Ten VIP Values (eV) for 2,4-DPTTP

ab initio[#] 3-21G*	DFT DMol	Orbital Character
7.73	7.45	81a $\pi_{S1\text{-}S2}$, $\pi_{C4\text{-}C5}$, $\eta_{S3,C2}$
8.30	7.71	80a $\sigma_{S1\text{-}S2\text{-}S3}$
8.99	8.30	79a $\pi_{TTP\ ring}$, $\pi_{benzene}$
9.43	8.52	78a $\pi_{TTP\ ring}$, $\pi_{benzene}$
9.49	8.61	77a $\pi_{benzene}$
9.65	8.70	76a $\pi_{benzene}$
10.57	9.27	75a $\pi_{S1\text{-}C1,S3\text{-}C5}$, $\pi_{S2\text{-}C3}$
10.95	9.34	74a $\pi_{S1\text{-}S2\text{-}S3}$, $\pi_{C2\text{-}C3\text{-}C4\text{-}C5}$
12.59	10.37	73a $\sigma_{S1\text{-}S2\text{-}S3}$
12.65	10.56	72a $\pi_{S3\text{-}C5}$, $\pi_{S1\text{-}C1\text{-}C2}$

[#] ref. 13

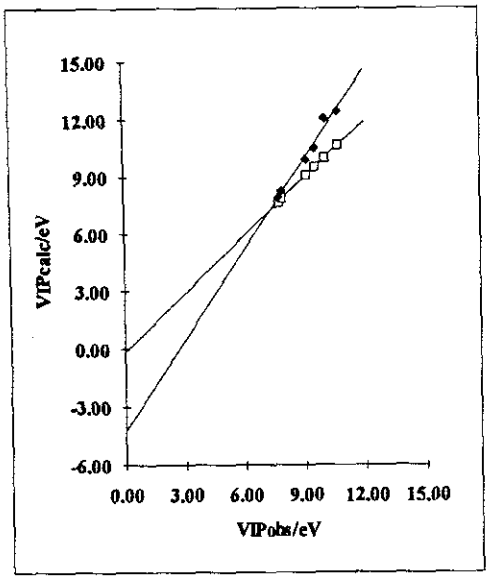

Fig. 4. Comparison of linear equations in terms of VIP_{obs} vs VIP_{cal} with VIP_{cal} calculated from ab initio (♦, ref. 13) and DFT methods (□) on 2,5-DMTTP.

values from DFT on two $\sigma_{S\text{-}S\text{-}S}$ MOs in 2,5-DMTTP and 2,4-DPTTP are nearly the same (2.65 eV for 2,5-DMTTP, 2.66 eV for 2,4-DPTTP) and comparable to the difference from experiment (2.80 eV for DMTTP[14]). The ab initio values differ more (by a factor 1.6) but are consistent in both molecules (4.21 eV for DMTTP, 4.29 eV for DPTTP). According to the result from 2,5-DMTTP, the experimental values should be very close to what calculated from DFT in Table 2.

CONCLUSION

This study demonstrates that DFT calculation can be used to derive the distribution of deformation density, net atomic charges and the VIPs. The results are as good as those produced from ab initio calculation, if not better. DFT is definitely suitable for calculations of charge density, and even advantageous for such studies of complicated molecules.

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