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THE ELECTRONIC STRUCTURE OF ARYL THIOL ESTERS

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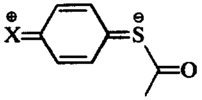
Abstract—A combination of experimental data and the CNDO/2-SCF-MO method are used to evaluate the importance of d-orbitals to the electronic structure of aryl thiol esters. The thioester group is calculated to withdraw electron density through σ and $2p_\pi - 3d_\pi$ bonding and donate by $p_\pi - p_\pi$ bonding. Electron donating substituents *para* to the thiol ester group cause the latter group to accept electron density regardless of d-orbital participation

Three types of experimental data have been rationalized in terms of the participation of nominally empty 3d-orbitals in the electronic structure of aryl thiol esters. First, Cilento[1] and later Baliah and Ganapathy[2] proposed that 3d-orbitals are important in the excited states of 4-substituted phenyl thiol acetates in order to explain the bathochromic shift of the ultraviolet spectrum caused by the introduction of electron donating groups *para* to the thiol ester group. Second, Baliah[3] and coworkers showed that the dipole moment for 4-N,N-dimethylaminophenyl thiol acetate is larger than the moment estimated from the moments for phenyl thiol acetate and N,N-dimethylaniline. These data have been cited as proof that electron density is transmitted from the electron donating group to the sulfur and oxygen atoms of the thiol ester via $2p_\pi - 3d_\pi$ bonding between sulfur and the adjacent C atoms, an effect, which has been represented by the charge separated valence bond structures 1 and 2.



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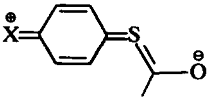


2

Third, Sheppard and Taft[4] have interpreted the downfield shift of ^{19}F resonance of 4-fluorophenylthiol acetate relative to the ^{19}F resonance of 3-fluorophenylthiol acetate as evidence for $2p_\pi - 3d_\pi$ electron withdrawing by the thiolester group. However, theoretical considerations suggest that valence expansion can occur when and only when the third row element without multiple bonds bears a formal positive charge.[5] Transmission of electron density from X to O and S will not necessarily demonstrate that 3d orbitals are involved in the electronic structure of aryl thiol esters.

In view of our interest in the photo-chemistry of aryl thiolesters[6] and the confusion surrounding 3d-orbital participation we decided to use a combination of experimental data and CNDO/2-SCFMO calculations in order to evaluate the mechanism of the electron withdrawal effect of the thiolester in the ground state and whether the group is electron withdrawing in the excited state.

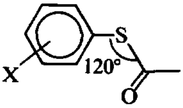
RESULTS AND DISCUSSION

The CNDO/2 method as formulated by Pople *et al.*[7a,b] was used without modification of parameters. Standard bond lengths as proposed by Pople[8] and a C—S bond distance of 1·76 Å were employed. The amino group was held planar in order to best approximate the resonance structures 1 and 2.

Examination of the total electron densities presented in Table 1 shows that the thiolacetate group is electron withdrawing. This effect is increased by inclusion of d-orbitals and by substitution of a *para*-amino group regardless of d-orbital participation. Substitution of a fluoro group *para* or *meta* decreases the electron withdrawing power of the thiolester group, the latter more so.

Three distinct bonding types must be considered—(1) σ—, (2) $3p_\pi - 2p_\pi$—, and (3) $3d_\pi - 2p_\pi$ bonding. Table 2 shows that when d-orbitals are excluded from the calculation, the thiolester group withdraws electron density via σ-bonding while donating π electron density to the benzene ring. However, when d-orbitals are included in the basis set the $3p_\pi - 2p_\pi$ electron donation is more than offset by electron withdrawal via $3d_\pi - 2p_\pi$ bonding of sulfur. Strong π-electron donor groups such as fluoro or amino when substituted *para* to the thiol acetate group cause π electron density to be transferred to the latter group regardless of d-orbital participation. Without d-orbitals the π-electron

Table 1. Total densities for thiol acetates



X	$q_X{}^c$	$\Delta q_{X(H-SCOCH_3)}$	q_{SCOCH_3}	$\Delta q_{SCOCH_3}(H-X)$
$H_a(F)$	−200	–	−90	–
$H_b(NH_2)$	−38	–	−115	–
m-F_a	−203	−3	−74	+16
m-F_b	−201	−2	−97	+18
p-F_a	−202	−2	−82	+8
p-F_b	−199	+1	−109	+6
p-NH_{2a}	−35	+3	−107	−17
p-NH_{2b}	−27	+9	−136	−21

[a] No d-orbitals.
[b] With d-orbitals.
[c] Densities are reported 10^3 actual value.

Table 2. π-Densities for thiol acetates

X	$q_{\pi-X}$	$\Delta q_{\pi-X(H-SCOCH_3)}$	$q_{\pi-SCOCH_3}$	$\Delta q_{\pi-SCOCH_3}(H-X)$
$H_a(F)$	1·9511	—	+0·0298	—
$H_b(NH_2)$	1·9050	—	−0·0425	—
m-F_a	1·9520	−0·0009	+0·0318	+0·0020
m-F_b	1·9529	−0·0018	−0·0373	+0·0052
p-F_a	1·9524	−0·0013	+0·0286	−0·0012
p-F_b	1·9492	+0·0019	−0·0469	−0·0044
p-NH_{2a}	1·9061	−0·0009	+0·0196	−0·0102
p-NH_{2b}	1·8979	+0·0081	−0·0575	−0·0150

[a] No d-orbitals.
[b] With d-orbitals

density of the fluoro and amino groups increases, with d-orbitals it decreases.

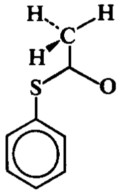
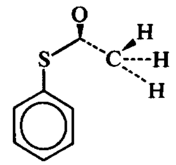
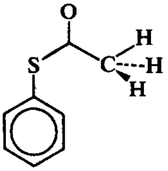
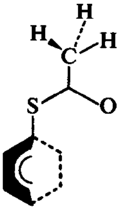
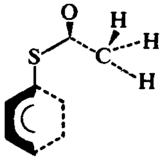
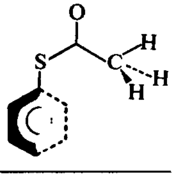
Inclusion of d-orbitals increases the electron density on sulfur and the carbonyl carbon while it decreases the density on oxygen. Sulfur and oxygen are negative regardless of d-orbital participation. Substitution of a *para* amino group increases the total electron density of all atoms of the thiol ester group with or without d-orbitals in the basis set.

Examination of the π-densities shows that the carbonyl oxygen is more negatively charged when d-orbitals are excluded. Sulfur is negatively charged with d-orbitals and positive without d-orbitals. A *para* amino group increases the π-electron density on sulfur and oxygen but decreases it on the carbonyl carbon regardless of d-orbital participation.

The charge distribution of phenyl and 4-aminophenylthiol acetate as a function of the relative orientation of the thiolacetate and phenyl groups was studied in order to further evaluate the effect of π-conjugation. Table 3 shows the thioester group is more electron withdrawing when the phenyl group is rotated out of π-conjugation with sulfur. Rotation of the acetyl group out of π-conjugation with sulfur which remains π-conjugated to the phenyl group causes no significant change in the withdrawing ability of the thiol ester group. Regardless of geometry or d-orbitals, substitution of an amino group causes an increase in the withdrawing ability of the ester, although nonplanar geometries with d-orbitals in the basis set exhibit a larger change in electron density on the thioester group. Rotation of the phenyl group out of conjugation with the thioester group increases the π-electron density at sulfur and oxygen when d-orbitals are excluded but carbon decreases in π-density. Table 4 also shows that when d-orbitals are included oxygen increases in π-density but sulfur can either increase or decrease depending on the orientation of the acetyl group with respect to the phenyl group.

Further evidence of the high degree of polarizability of sulfur in π-bonding comes from comparison of the π-electron densities of *meta* and *para*-fluorophenylthiolacetate. While a *para*-fluoro group increases π-density in the thiol ester group, a *meta*-fluoro group decreases the π-density. In the former case the carbon in the phenyl ring attached

Table 3. Effect of geometry on the total density

		q_H	q_{NH_2}	$\Delta q_{(H-NH_2)}$	
CH_3COS^a	I	−0·090	−0·107	−0·017	
CH_3COS^b		−0·115	−0·136	−0·021	
x^a		—	−0·035	+0·003	
x^b		—	−0·027	+0·011	
CH_3COS^a	II	−0·091	−0·104	−0·013	
CH_3COS^b		−0·106	−0·124	−0·018	
x^a		—	−0·033	+0·005	
x^b		—	−0·028	+0·010	
CH_3COS^a	III	−0·078	−0·091	−0·013	
CH_3COS^b		−0·104	−0·122	−0·018	
x^a		—	−0·033	−0·005	
x^b		—	−0·025	+0·013	
CH_3COS^a	IV	−0·130	−0·146	−0·016	
CH_3COS^b		−0·156	−0·188	−0·032	
x^a		—	−0·046	−0·008	
x^b		—	−0·031	+0·007	
CH_3COS^a	V	−0·134	−0·148	−0·014	
CH_3COS^b		−0·152	−0·177	−0·025	
x^a		—	−0·044	−0·006	
x^b		—	−0·030	+0·008	
CH_3COS^a	VI	−0·119	−0·135	−0·016	
CH_3COS^b		−0·147	−0·172	−0·025	
x^a		—	−0·044	−0·006	
x^b		—	0·030	+0·008	

[a] No d-orbitals.
[b] With d-orbitals.

to sulfur has excess π-density while in the latter that carbon is deficient in π-electron density.

The thioformate group shows a similar charge distribution profile as the thiolacetate group with *para*-fluoro and amino groups. In addition, we have considered the effect of a π-withdrawing group such as nitro when substituted *para* to the thioformate group. Tables 5 and 6 show that the nitro group causes a decrease in the π-electron density of the thioformate group as well as the total density regardless of d-orbital participation, although the loss of π-density from the thioformate group is larger when d-orbitals are included in the basis set. Further, oxygen and sulfur of the thioformate group decrease in π-density while the carbonyl carbon increases. Nevertheless, on an absolute basis the thioformate group is still electron withdrawing overall.

Clearly, the thioester group is electron withdrawing when considering the total electron density. The group donates electron density through $3p_\pi - 2p_\pi$ bonding and withdraws electron density through σ-carbon–sulfur bonding and $3d_\pi - 2p_\pi$ bonding. Therefore Baliah's and Ganapathy's

Table 4. Effect of geometry on π-densities of the thiolacetate group

Compound		$q_{O.H}$	$q_{O.NH_2}$	$\Delta q_O{}^c$	$q_{S.H}$	$q_{S.NH_2}$	$\Delta q_S{}^c$	$q_{C.H}{}^d$	$q_{C.NH_2}{}^d$	$\Delta q_C{}^c$
I	a	1·2835	1·2852	−1·7	1·9102	1·9194	−3·2	0·8056	0·8047	+0·9
	b	1·2410	1·2459	−4·9	2·0181	2·0294	−11·3	0·8182	0·8166	+1·6
III	a	1·2904	1·2921	−1·7	1·9181	−3·3	0·8004	0·7995	+0·9	
	b	1·2484	1·2538	−4·6	2·0139	2·0251	−11·2	0·8129	0·8109	+2·0
IV	a	1·2882	1·2889	−0·7	1·9374	1·9370	+0·4	0·8046	0·8039	+0·7
	b	1·2492	1·2510	−1·8	2·0107	2·0192	−8·5	0·8167	0·8149	+1·8
VI	a	1·3002	1·3010	−0·8	1·9364	1·9359	+0·5	0·7954	0·7945	+0·9
	b	1·2680	1·2680	0·0	2·0170	2·0158	+2·2	0·8032	0·8027	+0·5

[a] No d-orbitals.
[b] With d-orbitals.
[c] Δq's are reported 10^3.
[d] Carbonyl carbon.

dipole moment data, which shows the thioester group acquires electron density when substituted *para* with a dimethylamino group, does not prove that d-orbitals are involved in the ground state bonding of aryl thioesters since the thioester group can withdraw electron density via σ-bonding as well as $3d_\pi - 2p_\pi$ bonding. Taft's and Sheppard's ^{19}F NMR data for fluorothiolacetate should provide a more definitive test of the presence of $3d_\pi - 2p_\pi$ bonding. However, consideration of the Taft-Brownlee[9] plot of $10^4\Delta q^F(\pi)$ vs. $\int_{m-x}^{p-x}$ shows that the point for the thiolacetate group without d-orbitals, while below the line, is slightly closer to the line than the point for the same group with d-orbitals, although the latter point is above the line. Despite the small but positive $\sigma_{R_0} = 0{\cdot}01$ reported by Taft and Sheppard the ^{19}F NMR data is at best equivocal evidence for $3d_\pi - 2p_\pi$ bonding.

We next turn our attention to the excited state of aryl thiol esters. The electronic transitions appear to be of the $\pi \rightarrow \pi^*$ type. Table 7 summarizes the effect on the electronic distribution obtained by

Table 5. Total densities[c] for thiol formates

X	q_X	$\Delta q_{X(H-SCOH)}$	q_{SCOH}	$\Delta q_{SCOH}(H-X)$
H_a	—	—	−94	—
H_b	—	—	−112	—
F_a	−202	−2	−75	+19
F_b	−199	+1	−105	+7
NH_{2a}	−34	+4	−96	−2
NH_{2b}	−25	+13	−129	−17
NO_{2a}	−204	0	−45	+49
NO_{2b}	−196	+8	−72	+40

[a] No d-orbitals.
[b] With d-orbitals.
[c] Densities are reported 10^3.

Table 6. π-Densities for thiol formates

Atom[c]	q_H	q_F	$\Delta q_{(H-F)}$	q_{NH_2}	$\Delta q_{(H-NH_2)}$	q_{NO_2}	$\Delta q_{(H-NO_2)}$
O_a	1·2341	1·2330	+1·1	1·2370	−2·9	1·2267	+7·4
C_a	0·8066	0·8097	−3·1	0·8066	0·0	0·8146	−8·0
S_a	1·9269	1·9282	−1·3	1·9304	−3·5	1·9214	+5·5
OCS_a	+0·0324	+0·0291	−3·3	+0·0260	−6·4	+0·0372	+4·9
O_b	1·1970	1·1956	+1·4	1·2020	−5·0	1·1862	+10·8
C_b	0·8196	0·8210	−1·4	0·8171	+2·5	0·8265	−6·9
S_b	2·0222	2·0263	−4·1	2·0340	−11·8	2·0124	+9·8
OCS_b	−0·0388	−0·0429	−4·1	−0·0531	−14·3	−0·0251	+13·7
F_a	1·9511	1·9540	−3·9	—	—	—	—
F_b	—	1·9509	+0·2	—	—	—	—
H_2N_a	1·9050	—	—	1·9057	−0·7	—	—
H_2N_b	—	—	—	1·8978	+7·2	—	—
O_2N_a	4·0331	—	—	—	—	4·0369	−3·8
O_2N_b	—	—	—	—	—	4·0320	+1·1

[a] No d-orbitals.
[b] With d-orbitals.
[c] Densities listed for atoms indicated; subscripts on q refer to the substituent.

Table 7. Excited state electronic structure

	$\Delta q_{C,H}$[c]	$\Delta q_{C,NH2}$[c]	$\Delta q_{C,NO_2}$[c]
CH_3COS_a	0·4482	0·3492	—
CH_3COS_b	0·2019	−0·1138	—
$HCOS_a$	0·6558	—	0·6868
$HCOS_b$	0·2740	—	0·5241
NH_{2a}	0·3539	0·1708	—
NH_{2b}	—	0·0978	—
NO_{2a}	0·5090	—	−0·4461
NO_{2b}	—	—	−0·3263

[a] No d-orbitals.

[b] With d-orbitals.

[c] Positive sign means group listed donates electron density upon promotion of one electron.

promotion of one electron from the highest occupied π molecular orbital to the lowest unoccupied π molecular orbital. The thioester group is electron donating in all situations with the exception of one – when the thioester group is *para* to the amino and d-orbitals are included in the calculation. The amino group is electron donating in aniline in the excited state. When a thioester group is substituted *para* to the amino group the amino group is still electron donating but less so than in aniline particularly when d-orbitals are included in the calculation. While the nitro group is electron donating in the excited state of nitrobenzene according to calculations, it is electron withdrawing when a thioformate group is substituted *para* to the nitro group regardless of d-orbital participation.

Jaffe and Orchin[10] have shown that when a benzene ring is substituted[1,4] by two distinct groups which are of opposite electronic effect, i.e. one electron donating, one withdrawing, the maximum of the longest wavelength absorption will appear red shifted from the maximum calculated from the sum of the differences between the maxima of the two monosubstituted derivatives. Further, when the substituents are of the same electronic effect then the maximum will be the calculated sum or slightly blue shifted.

Examination of Table 8 shows that for 4-N,N-dimethylaminophenylthiol acetate the observed displacement is less than the calculated sum while for 4-nitrophenylthiol acetate the observed displacement is slightly larger than the calculated sum. Therefore, the thioacetate group is slightly electron donating and d-orbitals are not important in the excited state of phenylthiol esters as proposed by Cilento and Baliah.

Crandall and Olguin[12,13] have shown that a relationship exists between the degree of red shift on the absorption maxima of *para* substituted nitrobenzenes and anilines caused by polar solvent such as dioxane and the electron donating ability of the substituent. We have examined the solvent effect on the absorption maxima of a series of *para*-substituted phenylthiol acetates. Table 9 shows the results in a variety of solvents. For *para*-nitrophenylthiol acetate the red shift in terms of stabilization energy on going from cyclohexane to dioxane is similar to that observed for *para*-nitrobenzoic acid and smaller than that observed for nitrobenzene or *para*-N,N-dimethylnitroaniline. These data apparently show the thiolacetate group to be electron withdrawing in the excited state, a

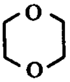
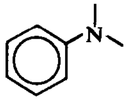
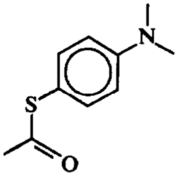
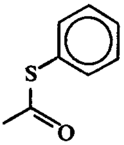
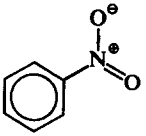
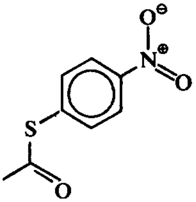
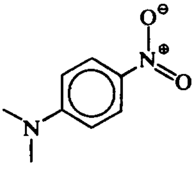
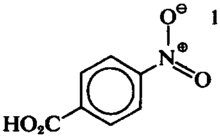
Table 8. Predicted and observed UV shifts for thiol acetates

A	Displacement mμ for A	B	Displacement mμ for B	Calc. Sum	Obs. Displacement
$(CH_3)_2N$	49	NO_2[10]	50	99	162
$(CH_3)N$	49	$CH_3\overset{\mathrm{O}}{\overset{\Vert}{C}}S$	27	76	67
$CH_3\overset{\mathrm{O}}{\overset{\Vert}{C}}S$	27	NO_2[10]	50	77	82
$CH_3\overset{\mathrm{O}}{\overset{\Vert}{C}}NH$[a 10]	38·5	NO_2[10]	56·5	95	112·5
CO_2H[b]	26·5	NO_2[10]	65	91·5	61
CH_3O[a 10]	13·5	$CH_3\overset{\mathrm{O}}{\overset{\Vert}{C}}$[10]	42	55·5	73
CH_3O[a 10]	13·5	$CH_3\overset{\mathrm{O}}{\overset{\Vert}{C}}S$	25	37·5	36
CH_3S[11]	51	$(CH_3)_2N$	49	100	68

[a] Ethanol.

[b] Water.

Table 9. Solvent effect on UV maxima of thiol acetates

Compound	 λ max mμ	 λ max mμ	ΔE kc/m	CH_3CN λ max mμ	ΔE kc/m	CH_3CH_2OH λ max mμ	ΔE kc/m
	297·5	300	−0·9	301	−1·2	297	+0·1
 2	270	275	−1·9	177	−2·6	275	−1·9
 3	230	—	—	227	+1·6	227	+1·6
 12, 14	253	260	−3·0	261	−3·5	260	−3·1
 15	285	290	−1·8	291	−2·4	290	−1·8
 12	365	382	−5·5	—	—	—	—
 12	253	257	−1·76	—	—	—	—

conclusion, which is at variance with other experimental evidence and the prediction based on the CNDO/2-SCF-MO method.

However, the solvent effect observed for *para*-N,N-dimethylaminophenylthiolacetate, while somewhat larger than for N,N-dimethylaniline, is not nearly as large as that for *para*-N,N-dimethylaminonitroaniline. The observed red shift is not large enough to be construed as evidence for the importance of quinoid structures 1 and 2 in the excited state and hence d-orbital participation.

In summary, there are two questions of importance—(1) whether a thiolester group is electron withdrawing or donating and (2) whether electron withdrawal by a thiolester constitutes evidence for valence expansion through d-orbital participation.

A corollary to question two is whether demonstration of π-electron withdrawal is evidence for $d_\pi - p_\pi$ bonding.

The evidence, experimental and theoretical, shows the thiol ester group is electron withdrawing in the ground state, a result, which seems to be consistent with or without d-orbital participation. However, if we accept Taft's σ_R value as evidence for π-electron withdrawal by the thioester group it does not follow that $d_\pi - p_\pi$ bonding is occurring. While CNDO/2 method does support the notion that π-electron withdrawal occurs by $d_\pi - p_\pi$ bonding it is also possible that sulfur could engage in $p_\pi - p_\pi$ electron withdrawal given the fairly large atomic radius of sulfur and hence small electron-electron repulsion.

With the exception of the solvent effect on *para*-nitrophenylthiol acetate there is no evidence that the thiolacetate group is electron withdrawing in the excited state. Therefore d-orbitals are probably not important in the excited state electronic structure.

EXPERIMENTAL

UV spectra were taken on a Cary Model 14 scanning spectrophotometer. All solvents except ethanol were Matheson spectroquality reagents. The thiol esters were prepared according to literature procedures and gave one peak in the gas chromatogram taken on a Hewlett-Packard Model 700 gas chromatograph fitted with 15% SE-30 silicon gum rubber and 10% Carbowax 20M.

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