Table III. NMR Data for Hydrazones in CCl_4[a]

1[11]	TMP: $(CH_3)_2$ 0.7 (s); $(CH_3)_2$ 1.07 (s); $(CH_2)_3$ 1.54 (m, broad) $=CMe_2$: CH_3 1.87 (s); CH_3 1.88 (s)
2[11]	TMP: $(CH_3)_4$ 1.02 (s); $(CH_2)_3$ 1.5 (m, broad) $=CH_2$: 7.07 (d) and 6.70 (d) (J = 14)
3	TMP: $(CH_3)_4$ 0.95 (s); $(CH_2)_3$ 1.5 (m, broad) $=CHCH_3$, 2.0 (d, J = 5.6); $=CHCH_3$, (q, J = 5.6)
4	TMP: $(CH_3)_2$ 0.80 (s, broad); $(CH_3)_2$ 1.18 (s, broad); $(CH_2)_3$ 1.58 (m, broad) $=C(CH_3)C_6H_5$, 2.38 (s); $=C(CH_3)C_6H_5$ 7.3 (m, 3 H), and 7.8 (m, 2 H)
5	TMP: $(CH_3)_4$ 0.95 (s); $(CH_2)_3$ 1.52 (m, broad) $=C(CH_2)_3$: 2.9 (m, 4 H) and 2.06 (m, 2 H)
6	TMP: $(CH_3)_4$ 1.0 (s) $(CH_2)_5$ 1.5 (m, broad); $(CH_2)_2$ 2.5 (m)
7	TMP: $(CH_3)_2$ 0.65 (s); $(CH_3)_2$ 1.04 (s) $(CH_2)_6$ 1.5 (m, broad); $(CH_2)_2$ 2.5 (m)
8	TMP: $(CH_3)_2$ 0.75 (s); $(CH_3)_2$ 1.07 (s) $(CH_2)_7$ 1.5 (m); $(CH_2)_2$ 2.56 (m)
9	TMP: $(CH_3)_2$ 0.75 (s); $(CH_3)_2$ 1.07 (s) $(CH_2)_8$ 1.5 (m); $(CH_2)_2$ 2.5 (m)
10	TMP: $(CH_3)_2$ 0.7 (s); $(CH_3)_2$ 1.07 (s) $(CH_2)_{12}$ 1.5 (m); $(CH_2)_2$ 2.5 m

[a] Probe temperature. Chemical shifts in ppm downfield from Me_4Si. J is in Hz.

Spectral Studies. NMR spectra were recorded at 60 or 100 MHz on JEOL C-60-HL and JEOL PS 100 spectrometers, respectively. After each spectrum was recorded, the temperature was measured by placing a thermocouple in a dummy tube. When CHF_2Cl was used as the solvent, ordinary NMR tubes were sealed under vacuum at liquid nitrogen temperatures. Only occasionally did these tubes burst on warming to room temperature. The DNMR computer program[24] was used for line shape analysis.

The x-ray diffraction data were collected on a Siemens AED apparatus and the structure was resolved using a MULTAN computer program.[21]

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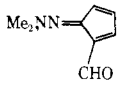
(9) The following hydrazones showed no sign of restricted rotation in their 100 MHz ^1H NMR spectra even at temperatures as low as −150 °C: $Me_2N{-}N{=}CH_2$; $Me_2NN{=}CMe_2$; $Me_2NN{=}CPh_2$; $(Me_2CH)_2NN{=}C(CH_2)_5$; $Me(Ph)NN{=}C(CH_2)_5$. This implies that $\Delta G^{\ddagger}$ for rotation is less than 6 kcal/mol.

(10) There is a rather odd exception to this statement. A. Mannschreck and U. Koelle (*Tetrahedron Lett.*, 863 (1967)) reported restricted rotation in



and attributed it to slow rotation around the N–N bond. However, since the corresponding compound lacking the CHO group did not show similar effects, one cannot rule out the possibility the motion was due to restricted rotation of the –CHO group.

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(16) As a general rule, the piperidyl methyls in the perpendicular conformation will be nonequivalent if the group attached to the piperidyl nitrogen lacks a symmetry axis on the NMR time scale. When such an axis is dynamically created (e.g., by fast N–N rotation in the hydrazones or by fast inversion at the NH_2 nitrogen in **11**) then the nonequivalence vanishes.

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(18) This comparison may not be completely appropriate since the decreased $\Delta G^{\ddagger}$ value for **13**, relative to the less hindered nitrosoamines **14**, . . . , **17**, is due mainly to repulsion between the two axial methyl groups.[5,8]

(19) The calculated line shapes exactly fit the experimental spectra for all the compounds listed in Tables I and II, *except* for **2**. In the case of **2**, there were small discrepancies which may be due to the fact that motions 2 and 3 are not sufficiently fast at −140 to −120 °C to be completely ignored. For this reason, only $\Delta G^{\ddagger}$ (measured from the coalescence temperature) is given for this compound.

(20) In all the cases in which $\Delta S^{\ddagger}$ was measured it was found to be negligible. For this reason $\Delta G^{\ddagger}$ (which can be determined more accurately than $\Delta H^{\ddagger}$) will be used as a measure of the rotational barrier.

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Electronic Properties of Aliphatic Xanthate Ions

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Abstract: The CNDO/2 method has been used to examine the electronic structure of aliphatic xanthate ions, especially by the participation of the 3d orbitals of sulfur. With the ASMO SCF method it is also applied to confirm three ultraviolet absorption peaks to be due to $n \rightarrow \pi^*$, $\pi \rightarrow \pi^*$, and $n \rightarrow \sigma^*$ transitions, respectively. The inductive effect of the polar groups in homologues of xanthic acids, carboxylic acids, and amines is transmitted to five, six, and three successive carbon atoms in their ionic forms, while the effect of fluorine in the fluorinated compounds is transmitted to five or more. The induced charges seem to alternate in a decaying manner. The total energy of a homologous series of a few compounds has an approximately additive property per CH_2 or CF_2 group.

Various organic compounds including the second row elements of the periodic table have recently attracted many experimental and theoretical chemists, who have in a systematic manner studied them. Organic sulfur compounds in this category are of great importance and interest not only from the point of their utilitarian aspects as rubber vulcanizers, pesti-

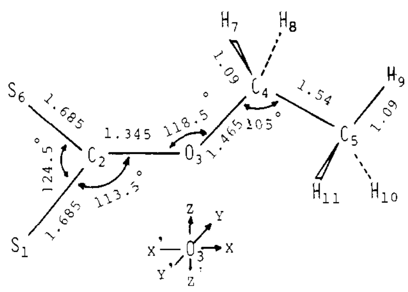

Figure 1. Coordinates of the ethylxanthate ion.

Table I. Bond Length and Bond Angle

Bond length, Å		Bond angle, deg	
Alkyl group			
C—C	1.54	∠CCC	112
C—H	1.09		
Carboxylic acid			
C=O	1.29	∠OCO	130
		∠OCC	115
		∠CCC	108
Amine			
N—H	1.032	∠NCC	108
N—C	1.465		
Fluoro compound			
C—F	1.33	$-CH_3$ $-NH_3$ $-CF_3$	Tetrahedral structure

cides, agricultural and medical reagents, and in the viscose industry, but also from such physicochemical points as their 3d orbital resonance, valence states, bond properties, steric effects, and reactivities.[1-4] Xanthates (*O*-alkyl dithiocarbonic salts), commonly known as sodium ethylxanthate ($C_2H_5OCS_2Na$), nickel ethylxanthate ($(C_2H_5OCS_2)_2Ni$), and so forth, have been empirically investigated in their reactivities, decomposition, absorption on metals or metal sulfides, and metal complexes.[5-6] However, xanthates or xanthic esters have not been elucidated in detail in their electronic features, though a few dithioates were calculated by the simple Hückel method.[7] It is, therefore, the purpose of this paper to discuss the electronic structure, the bonds, and the ultraviolet absorption spectra of ethylxanthate ion ($C_2H_5OCS_2^-$) or ethylxanthic acid ($C_2H_5OCS_2H$) by the LCAO method. The dissociation of ethylxanthic acid, 2,2,2-trifluoroethylxanthic acid ($CF_3CH_2OCS_2H$), and perfluoroethylxanthic acid ($C_2F_5OCS_2H$) are also compared on the basis of their bond energies and energy differences. The inductive effect of the xanthate skeleton ($-OCS_2$) in a series of xanthate ions ($C_nH_{2n+1}OCS_2^-$) as well as that of fluorine in a series of perfluoroxanthate ions ($C_nf_{2n+1}OCS_2^-$) and a 5,5,5-trifluoroamylxanthate ion ($CF_3C_4H_8OCS_2^-$) are argued in company with a series of carboxylate and aminium ions. Furthermore, we examine additivity of their total energies by the same level. Calculations were mainly carried out by the CNDO/2 method, but a few of them were done by the extended Hückel method and the ASMO SCF method for the purpose of comparing those ones. Both bond distances and bond angles of the organic compounds in Table I were determined from the compilation by Sutton,[8] except for the xanthate ions.

Results and Discussion

Electronic Structure of Ethylxanthate Ion. In order to calculate an ethylxanthate ion by the LCAO MO method, an example of its coordinate is represented in Figure 1 with reference to the configuration of arsenious xanthate,[9] antimonious xanthate,[10] nickel xanthate,[11] and potassium xanthate,[12] determined by means of the x-ray diffraction analysis. Figure 2 indicates the total energy of the ethylxanthate ion, where the coordinate of sulfur atoms changes as a function of angles, $\theta = \angle X'C_2S_6$, both the bond length and the bond angle being fixed as $S_1C_2 = S_6C_2 = 1.685$ Å and $\angle S_1C_2S_6 = 124.5°$. The minimum total energy (−65.0754 au) occurs around an angle ($\theta = 58°$) nearly coincident with Figure 1, while the total energies in the cases of the symmetrical position of both sulfur atoms for the x axis ($\theta = 62.25°$), the same atom population of both sulfur atoms (those of S_1 and S_6 are 6.586 e at $\theta = 56°$), and the symmetry plane (the xz plane) in the alkyl group to bisect the S-C-S angle on the coplane of the polar group are evaluated as −65.0744, −65.0746, and −65.0656 au, respectively. Then the ethylxanthate ion was calculated in the configuration of Figure 1.

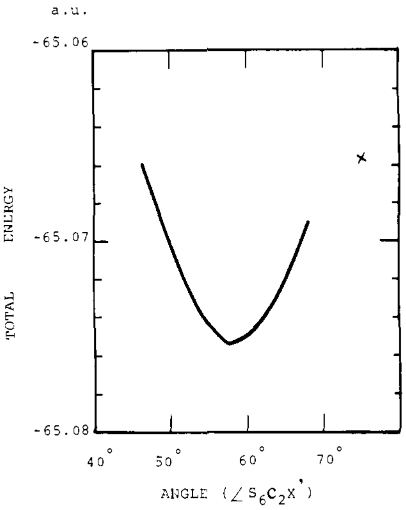

Figure 2. Total energy as a function of angles $\angle S_6C_2X'$ in CNDO/2-sp. A X sign indicates the total energy of the symmetry plane in the alkyl group to bisect the S-C-S angle on the coplane of the polar group in the ethylxanthate ion.

Since Longuet-Higgins[13] introduced the 3d orbitals of sulfur into the consideration of the thiophene molecule, Mulliken,[14] Moffitt,[15] Pauling,[16] and Jordan[17] have discussed the d-orbital participation on the elements belonging to the second row. Afterwards, Santry and Segal[18] calculated many molecules including the second row elements by the CNDO method, pointing out that the spd bonding gave a great influence on dipole moments, electronic structures, and bond properties of molecules. As the xanthate ion involves sulfur, oxygen, and carbon atoms in its polar group, it will be instructive to consider the ion from the viewpoint of the sp and spd bonding. A molecular diagram of the ethylxanthate ion in the extended Hückel (EH),[19] CNDO/2-sp (sp),[18,20] CNDO/2-spd′-(spd′),[18,20] and CNDO/2-spd (spd)[18,20] methods is given in Figure 3. Comparing EH with each CNDO/2, we can find that in the former the atom population of each element in the polar group gives a following order of O > S > C, in spite of an order of S > O > C in the latter. Furthermore, the EH calculation shows that electrons of carbon are greatly attracted to both sulfur and oxygen by the difference of their electronegativities to lead to the large separation of electron distributions on each atom. Tables II–V demonstrate the atomic orbital population and the bond order of the ethylxanthate ion. As seen in Table II, the sulfur atom receives a great share of the charge withdrawn from the central carbon atom, although oxygen is the more electronegative element. Of course, electrons on the sulfur atom distribute in a great part on its s and p orbitals, but in a small part on its d orbitals. The d-orbital contribution in the spd′ method tends to be too large, e.g., about 10% of the

Table II. Atomic Orbital Populations of Sulfur, Carbon, and Oxygen in the Polar Group of the Ethylxanthate Ion

	sp				spd′				spd			
Orbital	S_1	C_2	O_3	S_6	S_1	C_2	O_3	S_6	S_1	C_2	O_3	S_6
s	1.875	1.188	1.629	1.875	1.814	1.075	1.544	1.814	1.888	1.137	1.623	1.888
p_x	1.800	0.800	1.399	1.685	1.722	0.801	1.348	1.595	1.790	0.806	1.370	1.660
p_y	1.777	0.582	1.834	1.780	1.315	0.784	1.840	1.376	1.632	0.711	1.854	1.636
p_z	1.132	1.100	1.334	1.249	1.104	0.972	1.361	1.192	1.013	1.114	1.324	1.140
d_{z^2}					0.199			0.213	0.080			0.070
d_{zx}					0.163			0.168	0.065			0.074
d_{yz}					0.299			0.292	0.060			0.053
d_{xy}					0.033			0.075	0.009			0.017
$d_{x^2-y^2}$					0.049			0.088	0.009			0.016

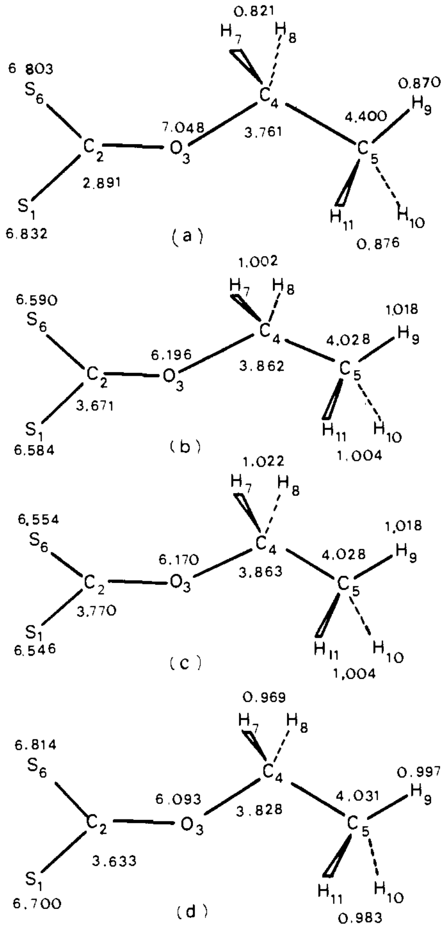

Figure 3. A molecular diagram of the ethylxanthate ion: (a) extended Huckel; (b) CNDO/2-sp; (c) CNDO/2-spd; (d) CNDO/2-spd′.

Table III. Bond Order Matrix for the Polar Group of the Ethylxanthate Ion in the sp Method

	C_2			
	2s	$2p_x$	$2p_y$	$2p_z$
S_1 3s	0.167	−0.099	0.0	−0.255
$3p_x$	0.261	0.036	0.0	−0.305
$3p_y$	0.0	0.0	0.562	0.0
$3p_z$	0.505	−0.306	0.0	−0.592
O_3 2s	0.214	0.451	0.0	0.025
$2p_x$	−0.406	−0.675	0.0	−0.020
$2p_y$	0.0	0.0	0.441	0.0
$2p_z$	0.008	0.064	0.0	0.165
S_6 3s	0.171	−0.129	0.0	0.240
$3p_x$	0.335	−0.053	0.0	0.381
$3p_y$	0.0	0.0	0.559	0.0
$3p_z$	−0.474	0.371	0.0	−0.498

Table IV. Bond Order Matrix for the Polar Group of the Ethylxanthate Ion in the spd′ Method

	C_2			
	2s	$2p_x$	$2p_y$	$2p_z$
$S_1$3s	0.139	−0.083	0.0	−0.220
$3p_x$	0.208	10.011	0.0	−0.321
$3p_y$	0.0	0.0	0.489	0.0
$3p_z$	0.452	−0.294	0.0	−0.558
$3d_{z^2}$	0.281	−0.172	0.0	0.235
$3d_{zx}$	0.197	0.161	0.0	0.020
$3d_{yz}$	0.0	0.0	0.444	0.0
$3d_{xy}$	0.0	0.0	0.105	0.0
$3d_{x^2-y^2}$	−0.008	0.097	0.0	−0.038
O_3 2s	0.191	0.395	0.0	0.019
$2p_x$	−0.388	−0.653	0.0	−0.023
$2p_y$	0.0	0.0	0.268	0.0
$2p_z$	0.006	0.046	0.0	0.151
S_6 3s	0.139	−0.106	0.0	0.201
$3p_x$	0.278	−0.073	0.0	0.385
$3p_y$	0.0	0.0	0.470	0.0
$3p_z$	0.429	0.349	0.0	−0.452
$3d_{z^2}$	0.221	−0.170	0.0	−0.246
$3d_{zx}$	−0.258	−0.110	0.0	0.013
$3d_{yz}$	0.0	0.0	−0.433	0.0
$3d_{xy}$	0.0	0.0	0.157	0.0
$3d_{x^2-y^2}$	0.024	0.105	0.0	0.012

total atom population of sulfur is due to the strong occupation of electrons on the $3d_{yz}$, $3d_{z^2}$, and $3d_{zx}$ orbitals, while it becomes about 3% in the spd due to the relative weak occupation of them on the 3d orbitals. An interesting feature of the atomic orbital population and the bond order is that they show the sulfur 3s orbital to be acting more as a lone pair orbital despite the result that the oxygen 2s orbital participates considerably in the bonding. From Tables III–V the π–π bonding seems to play a greater role on the sulfur–carbon bonding than on the carbon–oxygen bonding. A main effect on charge distributions concerning the inclusion of sulfur 3d orbitals is to increase π electrons of carbon and oxygen by donating them from sulfur to others with decreasing σ electrons of carbon and oxygen simultaneously. Though the increase of the π electrons of carbon surpasses the decrease of σ electrons of it in the spd method, the latter exceeds the former in the spd′. Consequently, the total back-donation occurs from sulfur to carbon in the spd method, whereas it occurs from carbon to sulfur in the spd′. This leads to the fact that we must make clear which method we are referring to when discussing the 3d-orbital

Table V. Bond Order Matrix for the Polar Group of the Ethylxanthate Ion in the spd Method

	C_2			
	2s	$2p_x$	$2p_y$	$2p_z$
S_1 3s	0.156	−0.088	0.0	−0.235
$3p_x$	0.240	0.034	0.0	−0.288
$3p_y$	0.0	0.0	0.588	0.0
$3p_z$	0.457	−0.286	0.0	−0.566
$3d_{z^2}$	0.224	−0.174	0.0	−0.050
$3d_{zx}$	0.124	0.058	0.0	−0.201
$3d_{yz}$	0.0	0.0	0.199	0.0
$3d_{xy}$	0.0	0.0	0.077	0.0
$3d_{x^2-y^2}$	0.018	0.049	0.0	0.064
O_3 2s	0.221	0.435	0.0	0.030
$2p_x$	−0.413	−0.663	0.0	−0.018
$2p_y$	0.0	0.0	0.368	0.0
$2p_z$	0.014	0.060	0.0	0.152
S_6 3s	0.159	−0.116	0.0	0.220
$3p_x$	0.308	−0.050	0.0	0.361
$3p_y$	0.0	0.0	0.585	0.0
$3p_z$	−0.429	0.346	0.0	−0.475
$3d_{z^2}$	0.190	−0.179	0.0	−0.022
$3d_{zx}$	−0.175	0.017	0.0	−0.202
$3d_{yz}$	0.0	0.0	−0.187	0.0
$3d_{xy}$	0.0	0.0	0.102	0.0
$3d_{x^2-y^2}$	0.037	0.038	0.0	0.095

participation on sulfur. Judging from the great charge change of sulfur with the inclusion of 3d orbitals, the feature derived from the spd′ method may be excessive. The decrease of the total electron densities of oxygen with 3d-orbital participation is likely due to the charge redistributions by polarization between carbon and oxygen. It should be also noted that among the π–π bonds occupying a large portion in the sulfur–carbon bond the $3d_\pi$–$2p_\pi$ bond order increases in the S_1–C_2 bond with a decrease in the S_6–C_2 bond in both the spd and spd′ methods.

Another interesting point arises from the consideration of the eigenvectors of molecular orbitals. In the sp method the highest occupied energy level (HOMO) may be a nonbonding-type orbital of sulfur and the second occupied one may be a π-type orbital of sulfur. On the other hand, the lowest vacant energy level (LUMO) appears to be a π-type orbital of carbon mixing π-type orbitals of sulfur and oxygen and the second vacant one appears to be a σ-type orbital of almost equivalently mixing sulfur, carbon, and oxygen. Under the condition of the 3d orbital inclusion in both the spd and spd′ methods, however, HOMO and the second occupied energy level become inverse; HOMO is a π-type orbital and the other a nonbonding-type orbital. This reversal is brought about by a strong mixing of the sulfur 3d in the nonbonding orbital, leading to the considerable stabilization of it.

Electronic Structure of Ethylxanthic Acid. The total energy of ethylxanthic acid is given in Figure 4 in various configurations, in which its minimum value exists around $\theta = 30°$ in the sp method or $\theta = 45°$ in the spd′; though a few cases with a proton attached to S_1 were calculated in the sp or the spd′, each total energy in convergence was higher than the minimum value in Figure 4 except the result that in the spd′ some cases happened to have no convergence. Calculations for ethylxanthic acid were, therefore, carried out at $\theta = 45°$. A molecular diagram in each method is illustrated in Figure 5. As the atom population of both sulfur atoms decreases to a great extent, electrons move from sulfur, much more from S_6 strongly interacting with a proton, to hydrogen due to decreasing σ electrons, mainly of p_x, on S_6 and π electrons, mainly of p_y, on S_1 from the atomic orbital bond population of sulfur in (Tables II and VI). We can see in a like manner that the carbon atom tends to increase the atomic orbital population of s, p_x, and p_y, instead of increasing that of p_z; moreover, the oxygen atom has just an inverse tendency. By Table VII a new bond formation between hydrogen and sulfur results in weakening the S_6–C_2 bond and strengthening the C_2–O_3 bond. Then, the 3d-orbital participation on sulfur contributes to enhancing the sulfur–carbon and sulfur–hydrogen bonds with reducing the carbon–oxygen one. As to the bond assignment of C=S and C–O in the infrared spectra,[21-25] it has remained ambiguous. Which wavenumber is correct for the bond assignment of C=S, $1020–1070^{-1}$ or $1140–1280^{-1}$? The bond strength of C=S is stronger than that of C–O in both the EH and spd′ methods from Table VII, whereas the order of those bond strengths is reversed in the sp and spd. So it cannot be concluded from this calculation which is a stronger bond. However, the bond strength of the C=S and C–O bonds gives a reverse order in a decaying manner, sp > spd > spd′ for C–O and spd′ > spd

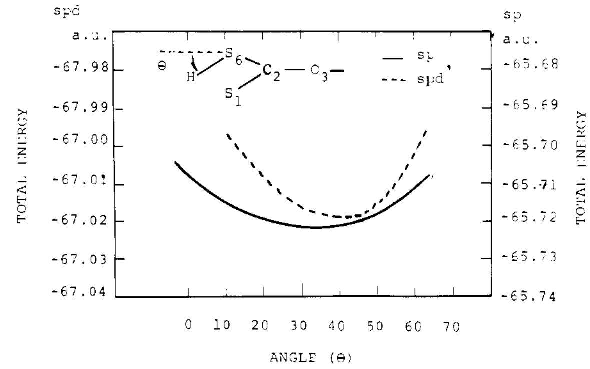

Figure 4, Total energy as a function of angles (θ).

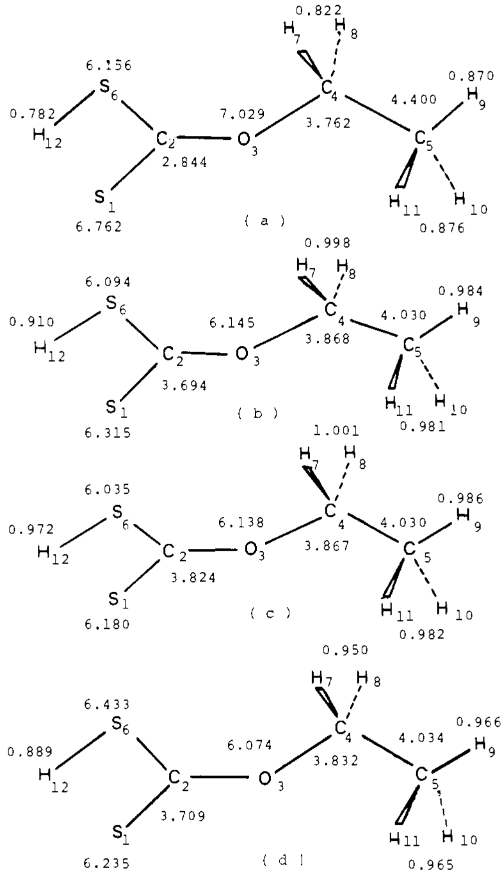

Figure 5. A molecular diagram of ethylxanthic acid: (a) extended Hückel; (b) CNDO/2-sp; (c) CNDO/2-spd; (d) CNDO/2-spd′.

Table VI. Atomic Orbital Populations of Sulfur, Carbon, and Oxygen in the Polar Group of the Ethylxanthic Acid

	sp				spd′				spd			
Orbital	S_1	C_2	O_3	S_6	S_1	C_2	O_3	S_6	S_1	C_2	O_3	S_6
s	1.881	1.212	1.622	1.837	1.827	1.083	1.542	1.801	1.889	1.151	1.614	1.846
p_x	1.808	0.845	1.328	1.232	1.808	0.841	1.278	0.960	1.813	0.849	1.303	0.943
p_y	1.623	0.634	1.793	1.927	0.763	0.896	1.844	1.887	1.234	0.806	1.834	1.938
p_z	1.003	1.004	1.402	1.098	1.166	0.889	1.410	0.973	0.977	1.018	1.388	0.995
d_{z^2}					0.173			0.167	0.081			0.060
d_{zx}					0.169			0.185	0.066			0.161
d_{yz}					0.237			0.279	0.095			0.043
d_{xy}					0.036			0.079	0.016			0.011
$d_{x^2-y^2}$					0.056			0.103	0.009			0.037

Table VII. Bond Energy (in atomic units) between Atoms in the Polar Group of the Ethylxanthate Ion and Ethylxanthic Acid

	Ion				Acid			
Bond	sp	spd′	spd	EH[a]	sp	spd′	spd	EH[a]
S_1-C_2	−0.794	−1.238	−0.991	0.970	−0.815	−1.254	−1.076	1.013
C_2-O_3	−1.158	−0.966	−1.095	0.582	−1.220	−1.009	−1.139	0.599
C_2-S_6	−0.800	−1.232	−0.996	0.986	−0.624	−1.074	−0.801	0.804
O_3-C_4	−0.991	−0.947	−0.989	0.436	−0.973	−0.932	−0.977	0.599
H_{12}-S_1					−0.003	−0.111	−0.007	−0.027
H_{12}-S_6					−0.415	−0.424	−0.479	0.768

[a] In EH, values are atomic bond populations.

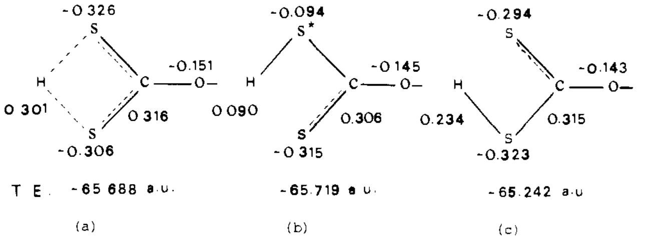

Figure 6. Total energy and charge distributions of each atom in the three forms of ethylxanthic acid in the sp method. Bond lengths are taken as S-H = 1.33 and S--H = 1.685 Å, respectively.

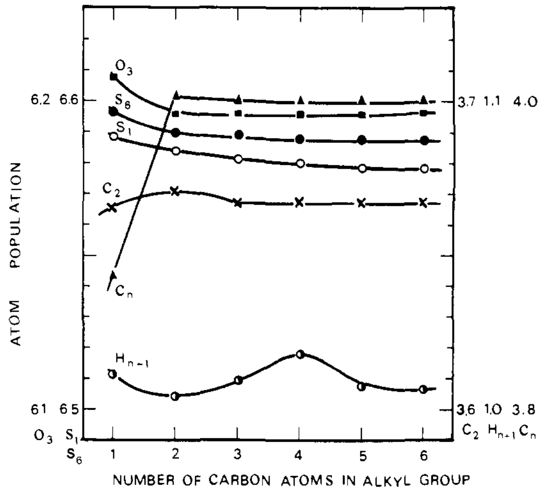

Figure 7. Change in atom population of each atom in a series of xanthate ions in the sp method. C_n and H_{n+1} mean carbon and hydrogen atoms in the methyl group.

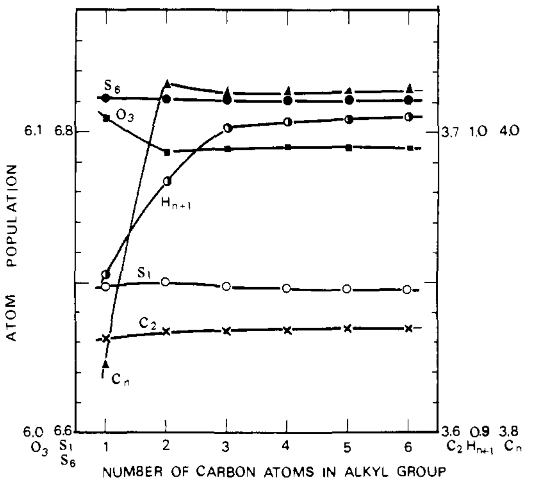

Figure 8. Change in atom population of each atom in a series of xanthate ions in the spd′ method. C_n and H_{n+1} mean carbon and hydrogen atoms in the methyl group.

> sp for C═S, only to be parallel to each π-bond character because of our empirical observation[21] that the frequency of the assigned C═S and C–O bonds shifts inversely in various xanthates; a xanthate with the higher frequency of the C–O bond indicates the lower frequency of the C═S bond. In Figure 6 the charge distribution of the polar group in ethylxanthic acid represented in the three forms, like xanthate complexes,[24] has a similar trend by neglecting the atom population of S* in b to be more neutral.

Electronic States of a Series of Xanthate Ions and Xanthic Acids. Atom populations of each element in a series of xanthate ions are illustrated in Figures 7–9. Their change seems to be alike in the sp and spd methods, but different in the spd′, as the number of carbon atoms in the alkyl group increases; e.g., the atom population of S_1 and S_6 tends to be in a decaying manner with the length of the alkyl group in the first two methods, while it behaves in a different way in the second one. Nevertheless, the atom populations in those cases are likely to remain almost constant from propylxanthate up to hexylxanthate ion. In HOMO and the energy gap (energy difference between LUMO and HOMO) of a series of xanthate ions and xanthic acids in Figure 10, the HOMO demonstrates a different tendency in each method. It is very interesting, however, not only for the energy gap to decrease with the hydrocarbon chain length, but also for its change to be smaller in the spd′ than in the sp, due to involving 3d orbitals. As shown in Table VIII,

Table VIII. Difference in Total Energies of a Series of Xanthate Ions and Xanthic Acids with and without the 3d Orbitals of Sulfur

	Ion				Acid	
	spd′ − sp	Ratio[a]	spd − sp	Ratio[a]	spd′ − sp	Ratio[a]
Methyl	−1.3668	2.4224	−0.3000	0.5317	−1.3007	2.2792
Ethyl	−1.3611	2.0916	−0.2995	0.4602	−1.2984	1.9757
Propyl	−1.3600	1.8443	−0.2995	0.4062	−1.2986	1.7458
Butyl	−1.3594	1.6496	−0.2995	0.3634	−1.2985	1.5636
Amyl	−1.3591	1.4924	−0.2995	0.3289		

[a] Ratio means (spd − sp) × 100/sp or (spd′ − sp) × 100/sp. In ethylxanthic acid spd − sp and ratio are −0.3189 and 0.4852, respectively. Total energies are expressed in atomic units.

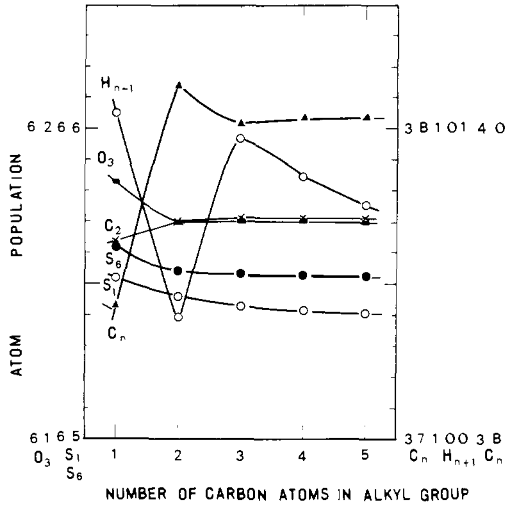

Figure 9. Change in atom population of each atom in a series of xanthate ions in the spd method. C_n and H_{n+1} mean carbon and hydrogen atoms in the methyl group.

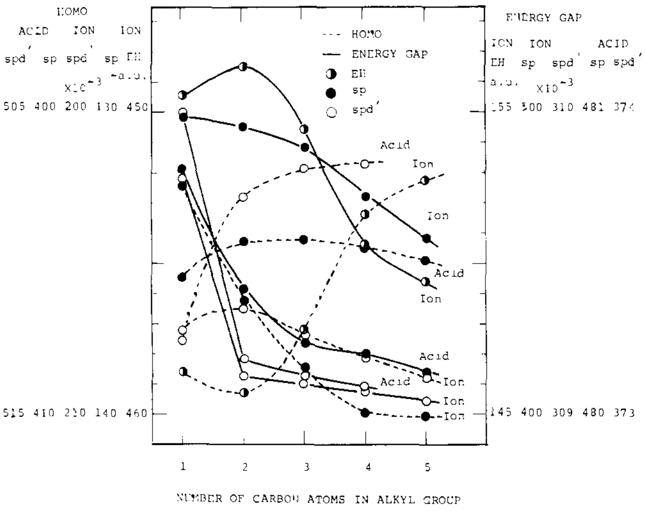

Figure 10. HOMO and energy gap of a series of xanthate ions.

the ethylxanthate ion appears to be more stable by the 3d orbitals of sulfur, whose contribution for the total energy can be estimated to be about 2% in the spd′ and 0.5% in the spd, respectively, with close relation to the weight of the 3d-orbital participation. In contrast to the effect of 3d orbitals on atom population (10% in the spd′ and 3% in the spd), the influence of those orbitals is small compared to the total energy. The 10% change seems to be a little overestimated, so that the percentage energy change in the spd′ will probably be around an upper limit to the energy lowering on the inclusion of those 3d orbitals.

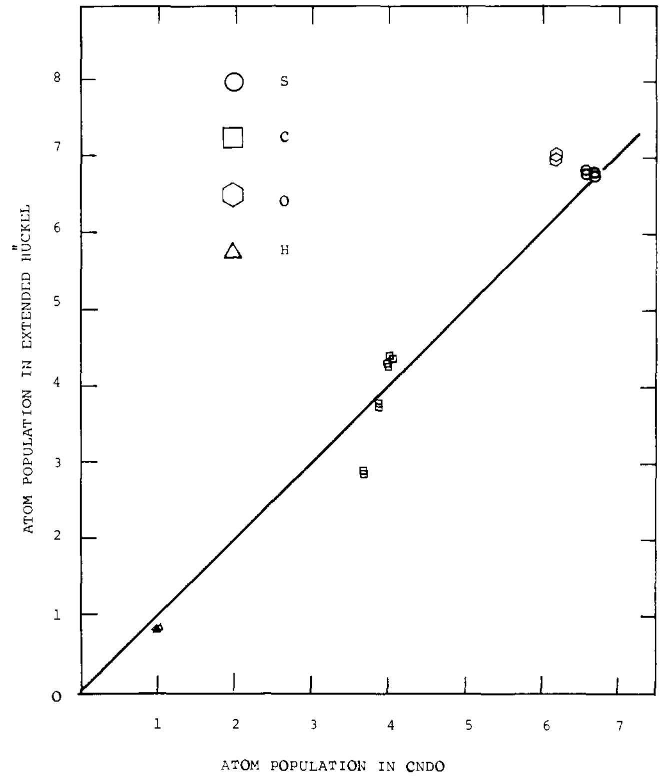

Figure 11. Correlation between atom population of each atom in ethylxanthate and amylxanthate ions in extended Hückel and that in CNDO/2-sp.

In ethylxanthate and amylxanthate ions Figure 11 shows a correlation between atom populations of each element by EH and the sp, which demonstrates a fair linear relationship as a whole in spite of a slight difference in individual atom populations.

Acid Strength. Acidity of acids and base strength have been studied on many conjugated compounds because they are particularly important for both inorganic and organic reactions, catalyzed reactions, and so forth. Longuet-Higgins[26] expressed an acid–base reaction as eq 1, and, after all, eq 2 can be obtained on the assumption of the constant energy terms of σ electrons,

$$B_1H^+ + B_2 \overset{K}{\rightleftharpoons} B_1 + B_2H^+ \qquad (1)$$

$$\delta\alpha(q_2 - q_1) = 2.3RT(pK_{a_1} - pK_{a_2}) \qquad (2)$$

where $\delta\alpha$ is a change of the Coulomb integral, and q is the π-electron densities. Equation 2 indicates a linear relationship between π-electron densities and pK values. This has been well known by a family of molecules like pyridine, quinoline, isoquinoline, acridine, and their amino derivatives.[26-27] In the case

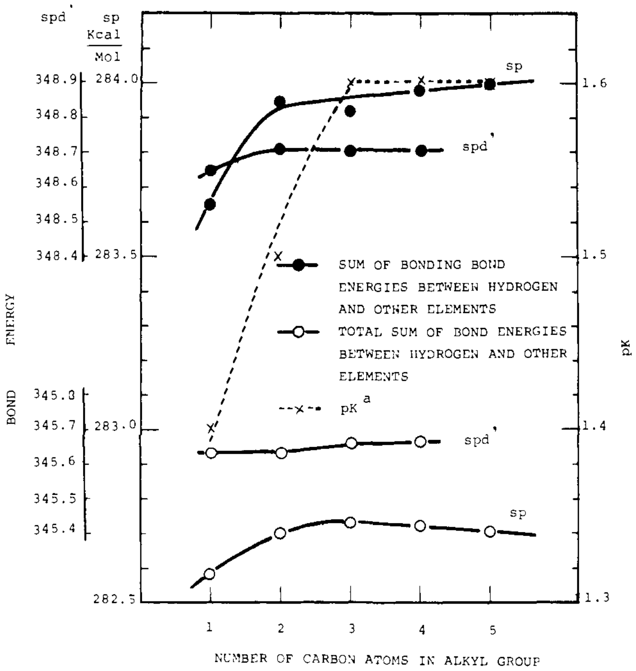

Figure 12. Relation between pK value and bond energy in a series of xanthic acids.

Table IX. Comparison of Dissociation Constant of Xanthic Acid with Energy Difference between Xanthate Ion and Xanthic Acid in the sp Method

	Energy difference[c]	pK_a[a]	K[b] × 10^2
Methyl	0.6458	1.4	3.4
Ethyl	0.6440	1.5	2.9
Propyl	0.6426	1.6	2.5
Butyl	0.6418	1.6	2.3
Amyl	0.6411	1.6	1.9

[a] See ref 28. [b] See ref 29. [c] Atomic units.

of aliphatic compounds, however, this relationship cannot be well established because of the small effects on the π system by the alkyl group. Another concept such as the bond energies of H–A, A being other elements connected with hydrogen, in a series of xanthic acids should be considered in order to explain their pK changes with the length of the hydrocarbon chain. Figure 12 shows a relation between empirical pK values[28-29] and calculated bond energies of H–A by the sp and spd′ methods. As to the acidity of a series of xanthic acids the following order is observed from the pK values: $CH_3 > C_2H_5 > C_3H_7 \geq C_4H_9 \geq C_5H_{11}$. Roughly speaking, the bond energy tends to increase from methylxanthic to propylxanthic acid, and then remains constant. This trend corresponds fairly well to the pK values of a series of xanthic acids. Also direct calculations of the energetics of the following transformation may be performed.

$$XH \rightarrow X^- + H^+$$

An order of acidity expected for this homologue turns out to be in disagreement with the empirical pK values, if we glance at the energy difference between the ionic species and the neutral species in Table IX.

Fluorinated acids are characterized by their highly acidic nature as compared to their hydrocarbon analogues. In addition, increase in acidic character is noted with increasing fluorine content.[30-31] Calculations for ethylxanthic acid, 2,2,2-trifluoroethylxanthic acid, and perfluoroethylxanthic acid by each method were similarly carried out on the basis of the bond energy and the energy difference. Results obtained are given in Tables X and XI. It is evident from this series that their acidity is parallel to the increase in fluorine content of fluorinated compounds.

Table X. Total Sum of Bond Energies between Hydrogen and Other Elements in Ethylxanthic and Fluorinated Ethylxanthic Acids[a]

	sp	spd′	spd
Ethyl	282.70	345.62	320.76
2,2,2-Trifluoroethyl	282.15	344.72	320.65
Perfluoroethyl	281.51	343.64	320.45

[a] Bond energy is expressed in kcal/Mol.

Table XI. Energy Difference between Fluorinated Ethylxanthate Ions and Acids[a]

	sp	spd′	spd
Ethyl	0.644	0.581	0.663
2,2,2-Trifluoroethyl	0.627	0.568	0.648
Perfluoroethyl	0.617	0.558	0.638

[a] Energy difference is expressed in an atomic unit.

Electronic Absorption Spectra. Out of three ultraviolet absorption lines of a sodium ethylxanthate solution, the weak peak appears at a wavelength of 380 nm (3.26 eV) and the strong peaks come out at 301 (4.12 eV) and 226 nm (5.49 eV), respectively.[32] A series of xanthates and xanthate derivatives give the similar absorption peaks.[33] The low intensity band around the 380-nm wavelength is very sensitive to solvents used. More polar and especially acidic solvents give rise to blue shifts, since the transition energy increases with an increase in the polarity of the solvent because of solvation and/or hydrogen bonding between the nonbonding electrons of the thio group and the solvent.[34] Thus, this longest wavelength can be ascribed to a transition of an electron from the sulfur lone pair to an antibonding π orbital, a n → π* transition. The second wavelength (301 nm) can be predicted as a π → π* transition, i.e., to an electron jump from the highest occupied π orbital to the lowest empty (antibonding) π level. As this intense absorption band shows little solvent effect, the assignment, a π → π* transition, may be in accordance with the empirical rule suggested by Kasha[35] and Sidman.[36] The lowest intense band is not easy and more speculative to be assigned due to the small solvent effect and small displacement in sulfuric acid, which suggests a second π → π* transition. However, many bands belonging to this type show mainly a blue shift when the solvent is changed from a nonpolar to a polar one.[37] This absorption band is, therefore, preferred by Shankaranarayana et al.,[33] by Mason,[38] and by Bergson[39] as a n → σ* transition. These absorption spectra in thione compounds have been extensively investigated by Janssen.[40,41]

In the foregoing EH calculation, the absorption band at 301 nm was very consistent with the π → π* transition, theoretically 275 nm. Others were in great disagreement with the assignments n → π* and n → σ*, respectively; both differences between theoretical and empirical values were about 100 nm. Table XII shows the calculated result of the ethylxanthate ion concerned with the singlet transition energies by the CNDO/2 and the ASMO SCF methods, neglecting the d-orbital participation.[42] Much improvement is achieved in the assignment of the two absorption bands at the wavelengths 380 and 227 nm, the latter of which is confirmed to be due to a n → σ* transition. Both the theoretical values of CNDO/2 and ASMO with CI are closer to the empirical values than those without

Table XII. Transition Energy of Ethylxanthate Ion by CNDO and ASMO without and with Configuration Interaction (10 CI's in Number)[c]

	n-π*	π-π*	n-σ*
X^b	3.26	4.12	5.49
log e	1.73	4.26	3.97
Transition energy by CNDO	5.38	7.32	8.54
Transition energy by CNDO CI	4.99	5.95	7.26
Oscillator strength	0.000	0.001[a]	0.012
Transition energy by ASMO	4.90	5.75	6.65
Transition energy by ASMO CI	3.75	5.69	6.20
Oscillator strength	0.000	0.365	0.125

[a] Oscillator strength shows 0.020 in case of 6 CIs in number. [b] See ref 32. [c] Transition energy is expressed in eV units.

CI. Moreover, the values of ASMO turn out to be better than those of CNDO/2, both with and without configuration interaction, respectively.

Inductive Effect. Knowledge of a functional group of an organic compound is one of the most important keys in order to understand reaction rates or equilibria. The inductive effect not dependent on conjugation with the mesomeric effect involving conjugation and with the steric effect has been discussed in attempting to correlate structure and reactivity of various organic compounds. Aliphatic xanthic acids, carboxylic acids, and amines appear in their ionic forms with the displacement of hydrogen in saturated hydrocarbons by such functional groups as -OCSS, -COO, and $-NH_3$, respectively, and consequently, their electronic rearrangement occurs in the alkyl group. It has been well known that this inductive effect tends to be in a decaying manner transmitted to the nonpolar skeleton by the screening effect of the CH_2 group with the number of carbon atoms in the alkyl group.[43] Thus, there is common interpretation of halides as an inductive effect type substitution leading to positive character in the saturated hydrocarbon, which diminishes steadily with increased distance down the chain, namely,

$$X^{\delta-} \leftarrow C^{\delta+} \leftarrow C^{\delta\delta+} \leftarrow C^{\delta\delta\delta+} \dots$$

Pople[44] challenged this interpretation by his statement that induced charges alternate in a decaying manner,

$$X^{\delta-} \leftarrow C^{\delta+} \leftarrow c^{\delta\delta-} \leftarrow C^{\delta\delta\delta+} \dots$$

In order to clarify this point the difference between atom populations of amylxanthic acid, caproic acid, and amylamine, in their ionic forms, and those of the parent hydrocarbon, pentane, is calculated in Figure 13, in which their polar groups are omitted. The induced charges tend not only to be in a decaying order transmitted to five successive carbon atoms in the xanthate ion, five or more in the carboxylate ion, and three in the aminium ion, but also to alternate their signs until three, four, and two carbon atoms in the same ions, respectively. Figure 14 presents the inductive effect on the carbon atom of the methyl group in a series of these ions, too. The screening effect by the hydrocarbon chain is rapid in xanthate and carboxylate ions as well as in aminium ions, which is different from and yet more reasonable than the calculated results by EH;[45] in EH the inductive effect in a series of aminium ions appears slowly, as far as ten successive carbon atoms in the alkyl group. In fact, this effect will stop at the fifth carbon away from the polar group of xanthate ions, the sixth in carboxylate ions, and the third in aminium ions, because 10^{-3} e should be very small. Such effects, which vanished beyond a certain number of carbons, make Langmuir's principle of independent surface action[46] strictly valid from the point of view of surfactants. This figure also gives us a somewhat interesting feature, partly because the similar slope of each line demonstrates the like rate of the screening effect almost independent of polar groups by every CH_2 skeleton, partly because the different signs of the carbon atoms in the methyl group come out concerning a positive inductive effect or a negative inductive effect; a negative sign means that electrons decrease as compared with those of the corresponding hydrocarbons. As shown in Figure 13, increase (+) of net electron densities of the hydrocarbon fragment in a carboxylate anion and decrease (−) in an aminium cation are coincident with conventional +*I* and −*I* effects, respectively, as a whole, but decrease in the xanthate anion results in a −*I* effect, which appears to be rather small in the sp method and greater in the spd′ by participating the 3d orbitals of sulfur. This point can be observed in Table XIII, too.

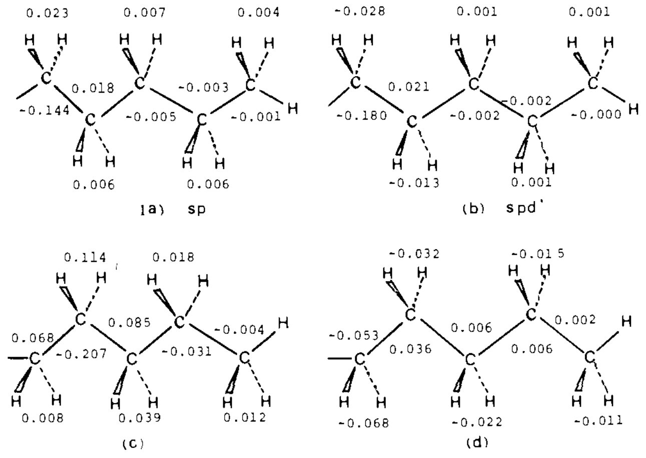

Figure 13. Difference between atom populations of amylxanthate ion, caproate ion, amylaminium ion, and those of pentane: (a), (b) amylxanthate ion; (c) caproate ion; and (d) amylaminium ion.

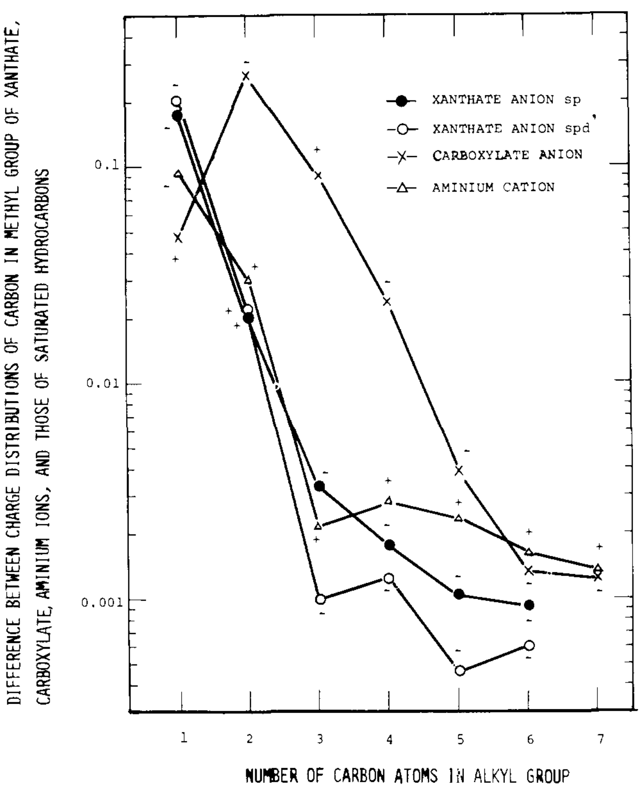

Figure 14. Inductive effect on carbon atom of the methyl group in a series of xanthate, carboxylate, and aminium ions.

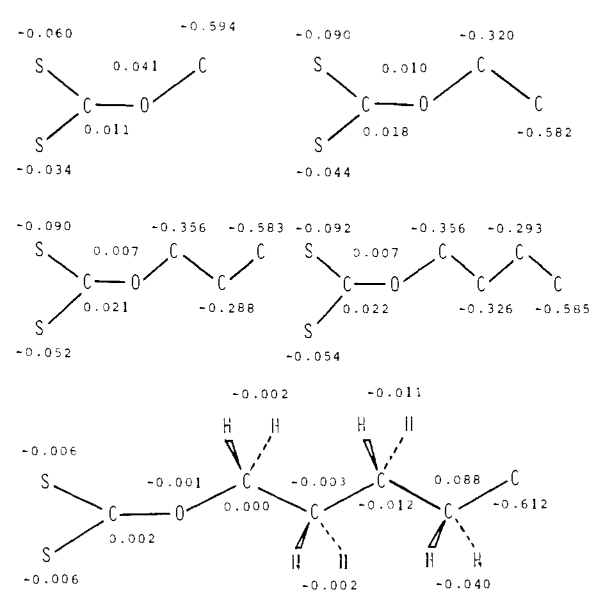

Figure 15. Difference between atom populations of a series of perfluoroxanthate ions, 5,5,5-trifluoroamylxanthate ion, and those of corresponding xanthate ions in the spd′ method. Fluorine atoms are omitted in this figure.

Table XIII. Difference between Net Atom Populations of Hydrocarbon Groups of a Series of Xanthate Ions and Those of Hydrocarbon Groups of a Series of Hydrocarbons

	Difference		
	sp	spd′	spd
Methyl	−0.072	−0.267	−0.074
Ethyl	−0.042	−0.243	−0.042
Propyl	−0.037	−0.240	−0.037
Butyl	−0.035	−0.239	−0.035
Amyl	−0.034	−0.239	−0.034
Hexyl	−0.034	−0.238	

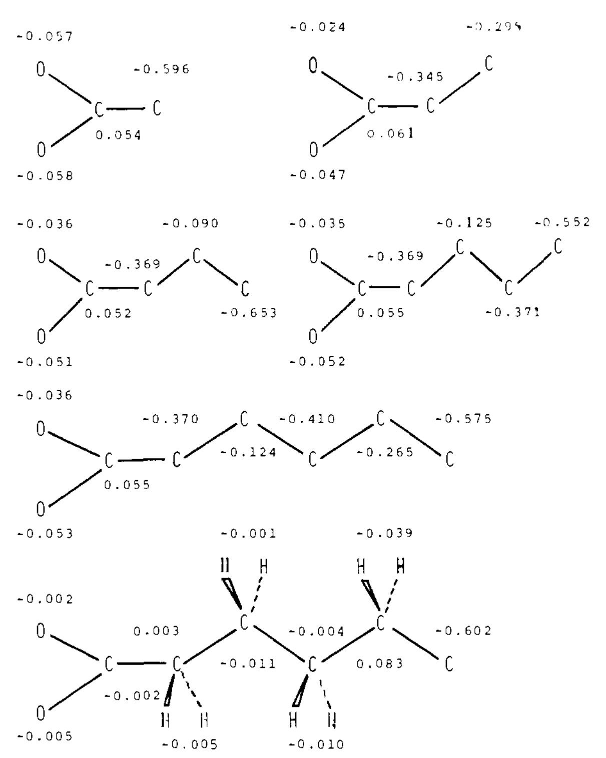

Figure 16. Difference between atom populations of a series of perfluorocarboxylate ions, 6,6,6-trifluorohexanoate ion, and those of corresponding carboxylate ions. Fluorine atoms are omitted in this figure.

The inductive effect is of particular importance in order to speculate the polarization effect of fluorine in fluorinated compounds. Figure 15 indicates the difference between atom populations of a series of perfluoroxanthate ions, 5,5,5-trifluoroamylxanthate ion, and those of corresponding xanthate ions. Figure 16 also shows the same difference in carboxylate ions. The charge distribution of carbon atoms linked with fluorine becomes much more positive due to the strong electronegativity of fluorine. Considering the influence of the fluorocarbon frame (C_nF_{2n+1}) on the polar groups, electrons may be withdrawn from them as a whole, to a greater degree as the fluorocarbon chain lengthens, though the latter trend seems to be vague in a series of perfluorocarboxylate ions. As to the charge distributions of the dithio group in the perfluoroxanthate ions, electrons decrease in sulfur while increasing in carbon and oxygen; there is such a similar tendency that they decrease in oxygen and increase in carbon in the perfluorocarboxylate ions. On the other hand, electrons of the oxygen atom in the dithio group as well as those of the carbon in the carboxylate group tend to decrease slightly in both trifluoro compounds. Tables XIV and XV give atomic orbital populations of 2,2,2-trifluoroethylxanthate and perfluoroethylxanthate ions, which change only a small quantity of both σ and π electrons as compared with the corresponding populations in Table II. Not only are net electron decreases of sulfur, indeed, due to small electron decreases of any other orbitals except the 3s orbital, but also net electron increases of carbon are due to small electron increases of any other ones except the $2p_x$ orbital. The decrease of electrons in the oxygen in the 2,2,2-trifluoroethylxanthate ion comes from that of the $2p_z$ and 2s orbitals, while its increase in the perfluoroethylxanthate ion arises from that of the 2s, $2p_x$, and $2p_y$ orbitals. In the 5,5,5-trifluoroamylxanthate and 6,6,6-trifluorohexanoate ions in Figures 15 and 16 the inductive effect of the fluorine atom decreases in its value due to the screening effect of the hydrocarbon chains as well as having an effect on five or more successive carbon atoms. In addition, the induced charges by the fluorine atom can be expected to alternate in a decaying manner. The influence of fluorine on the polar group is much greater in the perfluoroxanthate and perfluorocarboxylate ions than in the trifluoroxanthate and trifluorocarboxylate ones, so that the decrease of electrons in sulfur or oxygen may be greater in the former than in the latter, which is a factor to account for the increase in acidic character with increasing fluorine content, that is, readier release of a proton.

Additivity of Total Energies per CH_2 or CF_2. By analogy with the additive property of thermodynamic quantities such as entropy, heat of formation, and adsorption–desorption energies of homologous fatty acids and alcohols[47-49] as well as the van der Waals cohesive energies of long-chain hydrocarbons we have already pointed out additivity of total energies per CH_2 or CF_2 group in a homologous series of xanthic acids, perfluoroxanthic acids, carboxylic acids, perfluorocarboxylic acids, and amines, in their ionic forms, and saturated hydrocarbons on the basis of the EH method.[45] It is of particular interest to reexamine this property for the same homologues from the point of view of the CNDO/2 method. Figure 17 gives a good linear relationship between the total energy of each homologue and the number of carbon atoms in the alkyl group. Each slope of straight lines, i.e., the decreasing total energy per CH_2 or CF_2 group in the homologues, may be evaluated as 235.8 eV in xanthate ions (sp, spd′, and spd), 1703.1 eV in perfluoroxanthate ions (spd′), 231.7 eV in carboxylate ions, 1703.8 eV in perfluorocarboxylate ions, 235.7 eV in aminium ions, and 235.8 eV in the saturated hydrocarbons, respectively,

Table XIV. Atomic Orbital Populations of Sulfur, Carbon, and Oxygen in the Polar Group of the 2,2,2-Trifluoroethylxanthate Ion

	sp				spd′				spd			
Orbital	S_1	C_2	O_3	S_6	S_1	C_2	O_3	S_6	S_1	C_2	O_3	S_6
s	1.876	1.192	1.629	1.876	1.814	1.078	1.542	1.815	1.888	1.139	1.623	1.888
p_x	1.792	0.786	1.407	1.681	1.715	0.791	1.359	1.591	1.783	0.793	1.379	1.657
p_y	1.768	0.588	1.843	1.774	1.302	0.793	1.851	1.378	1.616	0.722	1.862	1.630
p_z	1.122	1.110	1.290	1.243	1.101	0.980	1.318	1.187	1.006	1.121	1.279	1.133
d_{z^2}					0.197			0.210	0.079			0.069
d_{zx}					0.161			0.166	0.065			0.073
d_{yz}					0.295			0.291	0.061			0.054
d_{xy}					0.032			0.073	0.010			0.017
$d_{x^2-y^2}$					0.045			0.084	0.009			0.016

Table XV. Atomic Orbital Populations of Sulfur, Carbon, and Oxygen in the Polar Group of the Perfluoroethylxanthate Ion

	sp				spd′				spd			
Orbital	S_1	C_2	O_3	S_6	S_1	C_2	O_3	S_6	S_1	C_2	O_3	S_6
s	1.876	1.197	1.644	1.876	1.815	1.082	1.560	1.815	1.889	1.141	1.638	1.889
p_x	1.786	0.770	1.432	1.672	1.709	0.777	1.388	1.587	1.777	0.777	1.406	1.652
p_y	1.760	0.596	1.847	1.760	1.312	0.803	1.840	1.357	1.608	0.737	1.867	1.606
p_z	1.116	1.122	1.273	1.228	1.093	0.990	1.316	1.182	1.002	1.130	1.261	1.120
d_{z^2}					0.195			0.206	0.079			0.068
d_{zx}					0.160			0.157	0.065			0.073
d_{yz}					0.296			0.285	0.062			0.055
d_{xy}					0.032			0.064	0.010			0.018
$d_{x^2-y^2}$					0.043			0.070	0.009			0.015

with a slight deviation of the methyl ones. The decreasing rate per CF_2 group appears to be much larger than that per CH_2 group due to the additional 18 valence electrons of an added CF_2 group compared with the six valence electrons of a CH_2 group. Here, we should pay attention to the result that the decrease of total energies for a series of carboxylate ions might be a little different due to the effect of the strong polar group on this molecular orbital basis, whereas it is almost independent of the polar group by the EH method. The more elaborate CNDO/2 method apparently includes the electron-electron repulsive terms in the Hamiltonian, so that the different effect of the different polar groups may, consequently, come out greater on the total energy of each homologue, especially on the first one of every series.

Concluding Remarks

Application of the CNDO/2 method to the calculation of the electronic structure of xanthate ions or xanthic acids sometimes presents a different effect in each method, even between the spd′ and the spd method, with or without a 3d parametrization due to a different estimation for the overlaps and the coulomb integrals. Then, we had better define with prudence which method we are referring to in order to discuss the 3d-orbital participation on sulfur. With a careful 3d parametrization this method should be successful in the explanation of d-orbital contribution to the electronic properties of molecules. The present calculations including the 3d orbitals of sulfur have thrown light on the importance to charge distributions, bond properties, total energies, and inductive effects of xanthate ions or xanthic acids; their moderate values appear in the spd calculation rather than in the spd′. In addition, this has elucidated p*K* changes in xanthic and fluorinated xanthic acids, additivity of total energies of xanthate ions, and the ultraviolet absorption spectra of the ethylxanthate ion as n → π^*, $\pi \rightarrow \pi^*$, and n → σ^* transitions with aid of the AMSO SCF method.

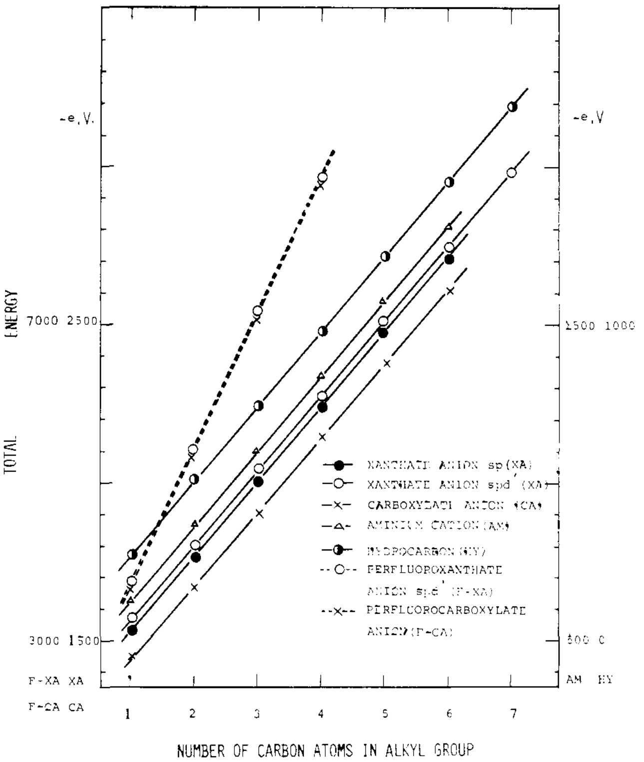

Figure 17. Additivity of total energy per CH_2 or CF_2 group.

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Stereoelectronic Properties, Stereospecificity, and Stabilization of α-Oxa and α-Thia Carbanions[1]

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Abstract: An ab initio study of the species **1**–**7** shows that carbanion stabilization by α-heteroatoms is subject to appreciable stereoelectronic effects. The following results are obtained: (a) stabilization of a carbanion by an adjacent sulfur atom is not due to (d-p)π bonding; (b) stabilization of $^{-}CH_2XZ$ increases in the series XZ = CH_2CH_3 < OH < OCH_3 < SH < SCH_3; (c) polarization of the electron distribution by the carbanionic charge is an important factor and stabilizes $^{-}CH_2SCH_3$ more than $^{-}CH_2CH_2CH_3$; (d) equatorial type carbanions (forms **e**) are much more stable than axial type carbanions (forms **a**) and this may explain stereochemical results in the carbanions derived from 1,3-dithiane systems; (e) these stereoelectronic effects may be interpeted in terms of a destabilizing (C^- lone pair, heteroatom lone pair) interaction in axial C^- and a stabilizing (C^- lone pair, antibonding σ* (X–Z) orbital) interaction in the equatorial C^- arrangement of a $^{-}CH_2XZ$ species; (f) the changes in bond lengths, orbital energies, and electronic distribution agree with this picture (for instance, in ^{-}CXC the length and overlap population of a X–C bond (X = O, S) respectively increase and decrease in the **e** forms (where X–C is antiperiplanar to the C^- lone pair) with respect to the **a** forms); (g) similar effects are present in the organolithium derivatives **3-Li**–**7-Li**.

Carbanions play an important role in chemical synthesis as well as in physical organic chemistry.[3] Control of stereochemistry in the formation of bonds to carbon and the rationalization of structural effects on carbanion properties represent two facets, synthetic on one hand and physicochemical on the other, of carbanion chemistry. A key position is occupied by carbanions $X–C^-$ formed in an α position to a heteroatom X. The present paper reports a theoretical study of the strong *stereoelectronic orientational effects* present in such carbanions, which should play a major role in the stereochemistry of carbanionic reactions.[3] Second row elements, in particular sulfur, are known to markedly increase the acidity of geminal C–H bonds[3] (see also extensive references in ref 4). To cite but two relatively recent discoveries, the Corey–Seebach synthesis of aldehydes via metalation of *m*-dithiane[5] and the so-called "contrathermodynamic" isomerization of bulky substituents from equatorial to axial position via metalation of *m*-dithiane substituted at C(2)[6] represent fascinating aspects of stabilization and stereospecificity in carbanion processes.

The fact that Me_3S^+,[8] $CH_2(2)$ in *m*-dithiane, and $HC(CH_2S)_3C\mathit{H}$[9] display a much higher C–H acidity than their oxygen counterparts, together with many other results, has been taken as evidence for specific (d-p)π stabilization of carbanions by the d orbitals[10] available on sulfur. Our earlier work on NH_2SiH_3 had demonstrated that the origin of the very low nitrogen inversion barrier cannot be ascribed to stronger N–Si (d-p)π conjugation in the planar vs. the pyramidal