NMR Spectroscopic Study of the Conformational Preference of Methoxycarbonyl and Methyl Substituted Thiophenecarbaldehydes. Possibility of a Hydrogen-Bond-Like Interaction between Formyl C-H and the Ester Carbonyl Group

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The predominance of planar C-H/O=C approached conformations in methyl 3-formyl-2-, 2-formyl-3-, and 4-formyl-3-thiophenecarboxylates was shown experimentally by the chemical shifts of the formyl protons, the unusually large $^1J_{CH}$ values of the formyl groups, and their infrared C-H and C=O absorptions. The stability of the C-H/O=C approached conformation was attributed to the hydrogen-bond-like interaction between the two groups. The considerably large positive bond population between non-bonded H/O and the additional charge separation indicated by the MNDO calculations supported the presence of the intramolecular hydrogen bond.

In the course of our investigations of thiophene derivatives, we have synthesized a variety of thiophenecarbaldehydes and studied their NMR spectroscopic behaviors. The ^{1}H and ^{13}C chemical shifts, as well as the coupling constants ($^1J_{CH}$ and $^3J_{HH}$), of several series of substituted 2- and 3-thiophenecarboxylic[1,2] and β-(2- and 3-thienyl)acrylic esters[3,4] were measured and correlated with each other and with the substituent electronic parameters. Some formyl esters were included in these series of thiophene derivatives. As they are capable of taking a C-H/O=C approached conformation in which an intramolecular C-H/O hydrogen bond may be persistent, the possibility of such intramolecular interaction was further examined.

The existence of intramolecular CH/O hydrogen bonds has been suggested by several investigations. Pinchas insisted on the existence of intramolecular C-H/O hydrogen bonds in *o*-nitrobenzaldehyde and related compounds on the basis of their unusually high formyl C-H frequencies.[5] On the other hand, hydrogen bonds involving C-H groups have been studied theoretically[6] and the important role of the electrostatic factor has been pointed out.[7] The formyl group is expected to be a strong C-H donor because the hydrogen is linked to a very electronegative carbonyl carbon atom; therefore, the C-H bond is expected to have some ionic character. Thus, the possibility of an intramolecular hydrogen bonding of this sort in these and related formyl esters will be discussed in this paper on the basis of NMR and infrared spectroscopic evidence and also on the basis of the theoretical consequences from molecular orbital calculations.

Experimental

Spectral Measurements. The thiophenecarbaldehydes were prepared according to the methods reported previously.[1,2,8-12]

The NMR spectra were recorded on a JEOL FX-90Q spectrometer. The samples were dissolved in chloroform-*d*, the concentrations of the solutions being adjusted to approximately 0.6 mol dm^{-3}. The chemical shifts were measured from the internal TMS reference at the probe temperature. The ^{13}C spectra were collected by using a 30° pulse, 16k data points, and a 4.5 or 5.0 kHz sweep width. The ^{13}C-^{1}H coupling constants were obtained by measurements using a pulse sequence which allowed us to observe the non-decoupled spectra while maintaining a full NOE. (Pulse conditions: 45° pulse, 3 repetition rates, 16k data points, and 450 Hz sweep width.)

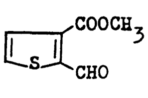
The infrared spectra were recorded on a Perkin-Elmer 257 spectophotometer in CCl_4.

MNDO Calculation.[13,14] The calculations were carried out by the use of the MOPAC program package[15] on a HITAC M-280H computer at the Computer Center of the University of Tokyo. A routine calculation gave the electronic energy, the density matrix (electron densities and bond orders), the eigen values and eigenvectors of MO's, and the other necessary quantities. The geometrical parameters of the stable conformations for MNDO calculations were cited from the Cambridge XDC Data Base whenever available. The s characters of the C-H bonds were computed from appropriate MO coefficients.

Results and Discussion

The ^{13}C NMR chemical shifts of substituted thiophenecarbaldehydes (**1a**—**4a**) were assigned on the basis of (i) the difference in the line intensities of the protonated and quarternary carbons, (ii) the substituent effect on the chemical shifts,[16,17] and (iii) the characteristics of the ^{13}C-^{1}H coupling constants, as reported previously.[18] The results are given in Tables 1—3.

A glance of the tables will show that the formyl $^1J_{CH}$ values of methyl *o*-formylthiophenecarboxylates are considerably larger than those of the other thiophenecarbaldehydes which have no neighboring methoxycarbonyl groups. Thus, the ^1J values of methyl 2-formyl-3-, 3-formyl-2-, and 4-formyl-3-thiophenecarboxylates (**1a**, **3a**, and **3b**) are 191.5, 188.9, and 187.5 Hz, respectively, larger than those of methyl 5-formyl-3-, 5-formyl-2-, and 4-formyl-2-thiophenecarboxylates (**1b**,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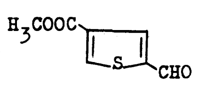
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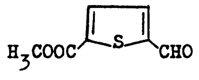
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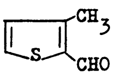
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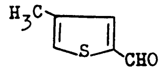
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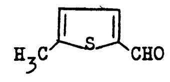
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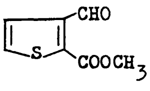
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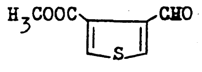
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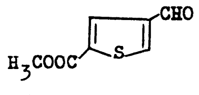
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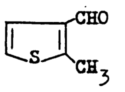
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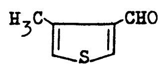
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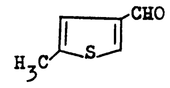

4c

1c, and **3c**) by ca. 10 Hz. We compared the ring $^1J_{CH}$'s in order to examine the effects of substituents. All the other one-bond spin-coupling constants, $^1J_{C(2)\text{-}H(2)}$, $^1J_{C(3)\text{-}H(3)}$, $^1J_{C(4)\text{-}H(4)}$, and $^1J_{C(5)\text{-}H(5)}$, are affected by the position and the nature of ring substituents to a considerably less extent than in the cases of the formyl $^1J_{CH}$'s of the *o*-formylesters **1a**, **3a**, and **3b**. The very remarkable fact about the $^1J_{CH}$ values of other aldehydes is that the $^1J_{CH}$'s of vicinally methyl-substituted thiophenecarbaldehydes **2a**, **4a**, and **4b** have almost the same values as those of other methyl-substituted thiophenecarbaldehydes void of a vicinal methyl group in spite of the fact that the formyl C–H group is located in the proximity of the methyl group on the neighboring carbon atom and is susceptible to the effect of steric compression. After all, the $^1J_{CH}$ values larger than normal were observed only with formylthiophenecarboxylates carrying formyl and alkoxycarbonyl groups on adjacent carbon atoms. This fact apparently contradicts the hypothesis that the larger $^1J_{CH}$ value is

Table 1. ^{13}C–H Coupling Constants of Substituted 2-Thiophenecarbaldehydes

Compound	$^1J_{CH}$/Hz				$^2J_{CH}$/Hz				$^3J_{CH}$/Hz				$^4J_{CH}$/Hz		
	$J_{CHO\text{-}CHO}$	$J_{C_3H_3}$	$J_{C_4H_4}$	$J_{C_5H_5}$	$J_{C_3H_4}$	$J_{C_4H_3}$	$J_{C_4H_5}$	$J_{C_5H_4}$	$J_{CHO\text{-}H_3}$	$J_{C_3\text{-}CHO}$	$J_{C_3H_5}$	$J_{C_5H_3}$	$J_{CHO\text{-}H_4}$	$J_{CHO\text{-}H_5}$	$J_{C_4\text{-}CHO}$
1a	191.5	—	174.4	188.0	—	—	4.2	6.6	—	—	—	—	1.0	1.0	0.5
1b	180.7	172.6	—	189.0	—	—	—	—	4.1	—	7.6	9.1	—	1.1	—
1c	181.2	170.7	173.8	—	4.6	4.6	—	—	3.2	—	—	—	0.8	—	—
2a	175.8	—	168.6	185.7	—	—	3.8	6.9	—	—	—	—	1.0	1.0	—
2b	177.2	165.8	—	182.9	—	—	—	—	3.7	0.6	8.6	9.9	—	1.3	—
2c	176.8	167.7	168.4	—	5.2	4.3	—	—	3.8	0.9	—	—	0.6	—	—

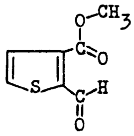
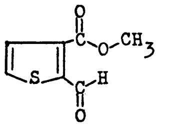
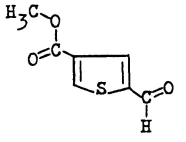
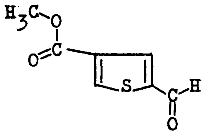
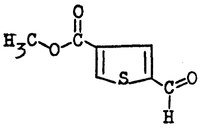
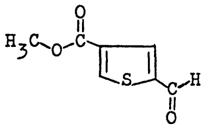
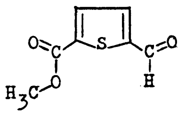
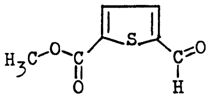
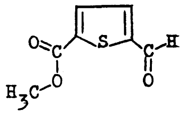
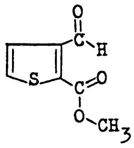
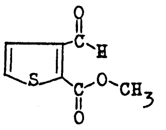
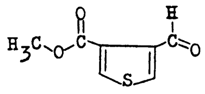
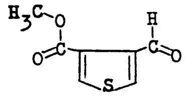
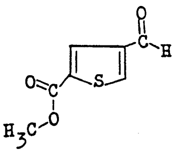
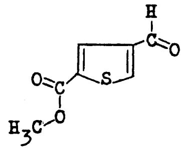
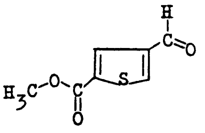
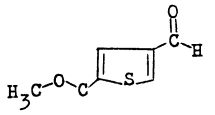
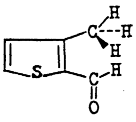
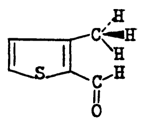
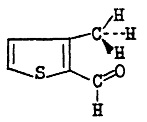
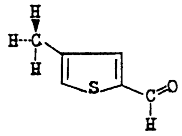
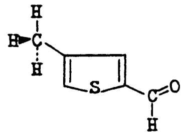
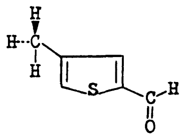
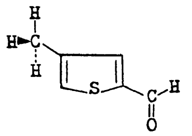
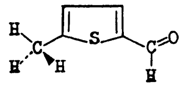
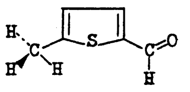
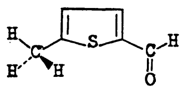
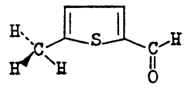
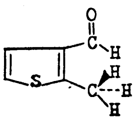
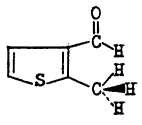
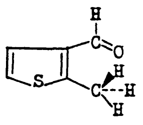
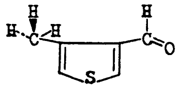
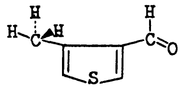
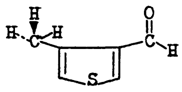
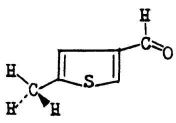
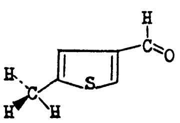
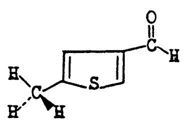
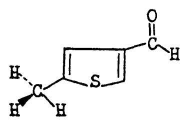
Table 2. ^{13}C–H Coupling Constants of Substituted 3-Thiophenecarbaldehydes

Compound	$^1J_{CH}$/Hz				$^2J_{CH}$/Hz		$^3J_{CH}$/Hz							
	$J_{CHO\text{-}CHO}$	$J_{C_2H_2}$	$J_{C_4H_4}$	$J_{C_5H_5}$	$J_{C_4H_5}$	$J_{C_5H_4}$	$J_{C_2\text{-}CHO}$	$J_{C_2H_4}$	$J_{C_2H_5}$	$J_{CHO\text{-}H_2}$	$J_{CHO\text{-}H_4}$	$J_{C_4H_2}$	$J_{C_5H_2}$	$J_{C_4\text{-}CHO}$
3a	188.8	—	173.9	187.8	4.0	6.8	—	—	—	—	1.5	—	—	3.7
3b	187.5	190.7	—	190.2	—	—	1.7	—	5.5	2.0	—	—	5.6	—
3c	177.5	186.5	174.1	—	—	—	1.5	9.5	—	1.7	3.3	7.9	—	3.0
4a	172.9	—	170.1	188.2	4.0	6.5	—	—	—	—	1.9	—	—	3.0
4b	173.8	184.9	—	184.5	—	—	1.5	—	5.6	3.8	—	—	5.5	—
4c	174.4	186.0	168.7	—	—	—	1.1	9.0	—	1.5	3.8	7.4	—	3.5

Table 3. ^{13}C NMR Chemical Shifts of Substituted Thiophenecarbaldehydes

Compound	δ_{CHO}	δ_{C_2}	δ_{C_3}	δ_{C_4}	δ_{C_5}	Others
1a	184.4	147.6	136.5	130.0	132.7	162.4($COOCH_3$) 52.4($COOCH_3$)
1b	182.5	144.5	136.1	134.7	140.2	162.1($COOCH_3$) 52.1($COOCH_3$)
1c	183.2	148.0	135.0	133.4	141.0	161.9($COOCH_3$) 52.7($COOCH_3$)
2a	182.1	137.6	147.3	131.8	134.2	14.0(CH_3)
2b	182.8	139.2	138.0	143.7	131.0	15.4(CH_3)
2c	182.5	142.0	137.3	127.2	151.6	16.1(CH_3)
3a	186.3	138.5	144.6	127.7	130.6	161.5($COOCH_3$) 52.7($COOCH_3$)
3b	186.5	133.2	140.7	132.2	135.2	162.6($COOCH_3$) 52.1($COOCH_3$)
3c	184.3	140.4	142.9	131.2	135.8	161.7($COOCH_3$) 52.5($COOCH_3$)
4a	184.5	151.6	137.1	127.4	122.6	13.5(CH_3)
4b	185.7	139.1	140.6	137.7	123.5	15.1(CH_3)
4c	184.8	135.5	143.2	122.8	142.0	15.1(CH_3)

Table 4. The Stable Conformers of Substituted Thiophenecarbaldehydes and Their Abundances (%)

Conformer	Abundance %	Conformer	Abundance %	Conformer	Abundance %	Conformer	Abundance %
	96		4				
	45		21		19		15
	65		27		8		
	95		5				
	91		9				
	52		20		18		10
	76		19		5		
	39		36		13		12
	38		36		13		13
	77		21		2		
	80		18		2		
	33		30		19		18

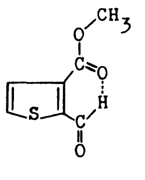
ascribable to the steric compression, though it may be relieved partly in the methylaldehydes (**2a**, **4a**, and **4b**) by taking the D conformer, in which the formyl hydrogen is located just in-between the two syn-clinal methyl hydrogens, in order to avoid the very large effect of steric hindrance; the reason for this anomaly might be found in the preferred C–H/O approached conformation of these aldehydes. Thus, an alternative interpretation which ascribes the larger $^1J_{\mathrm{CH}}$ value to a specific interaction became necessary in order to account for the phenomenon. By analogy with the cases of other hydrogen atoms attached to electronegative carbon atoms such as those in chloroform and in hydrogen cyanide, a hydrogen-bond-like interaction is suspected to be operating in these circumstances where the C–H group is opposed to the carbonyl oxygen and is capable of forming a planar six-membered chelate ring by the interaction.

Thus, MNDO calculations were carried out on these aldehydes in order to gain some insight into the nature of the interaction involved and the bonds concerned and in order to reproduce the stability of the C–H/O=C approached conformations. The stable conformations and their populations, as estimated by means of MNDO calculations are given in Table 4 for a series of methoxycarbonyl- and methyl-substituted thiophenecarbaldehydes. The populations of the C–H/O approached conformers (A—C) were calcu′lated to be 96, 95, and 91% for **1a**, **3a**, and **3b**, respectively; they were expected to be privileged with the aldehydes carrying a vicinal methoxycarbonyl group.

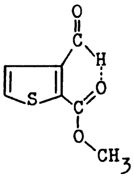
In contrast, the calculated energies of all the possible planar conformers of the other methyl formylthiophenecarboxylates which have no formyl group in the neighborhood of the ester group were nearly equal at the ambient temperature (i.e., the variation was less than, or comparable to, the kinetic energy for thermal motion, kT, at that temperature). Thus, the aldehydes can be expected to exist as a mixture of several conformers.

Table 5. Comparison of Observed and Calculated Percent *s* Characters of C–H Bonds for Substituted Thiophenecarbaldehydes

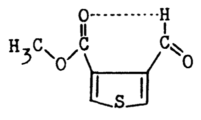
Compound	ρ_{CHO}/%	
	Obs	Calcd
1a	38.3	39.0
1b	36.1	38.0
1c	36.2	38.0
2a	35.2	37.8
2b	35.4	37.8
2c	35.4	37.8
3a	37.8	38.5
3b	37.5	38.5
3c	35.5	37.6
4a	34.6	37.4
4b	34.8	37.4
4c	34.9	37.4



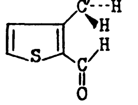
A



B



C



D

The percent s-character of the bonding orbital of the carbon atom which forms the formyl C–H bond (ρ_{CHO}) was estimated from the observed one-bond C–H coupling constants by the equation of Muller and Pritchard;[19] it is shown in Table 5, together with the values obtained from the MNDO calculations. The MNDO calculations gave a higher s-character of the carbon orbital for the C–H/O approached conformations of the *o*-formyl esters (**1a**, **3a**, and **3b**) than the others, accounting for the unusually large ^1J values observed with these aldehydes. Because of the high s-character of its bonding orbital, the formyl carbon becomes more electronegative, increasing the polarity of the formyl C–H bond. This should favor the attractive and hydrogen-bond-like interaction between the formyl C–H bond and carbonyl oxygen to a considerable extent. In turn, the attractive C–H/O interaction can be the driving force to force the *o*-formyl esters to take the C–H/O approached conformations (A—C).

The chemical shifts in Table 3 also suggest the predominance of the C–H/O approached conformations in the *o*-formyl esters. The ^{1}H chemical shifts of the formyl protons of **1a**, **3a**, and **3b** were observed at δ 10.65, 10.62, and 10.50, respectively.[1,2] These chemical shifts are about 0.7 ppm downfield from those of the non-adjacently functionalized formylthiophenecarboxylates. The downfield shift was observed also with the formyl ^{13}C chemical shifts of these aldehydes; it is ascribable to the strong magnetic anisotropy effect on the nucleus placed opposite to the robe of lone pair electrons of the carbonyl group.[20] In this way, the theoretically predicted predominance of the C–H···O approached conformers is supported experimentally by the unusually low ^{1}H NMR chemical shifts of the formyl protons of these aldehydes. The situation is very favorable to the hydrogen-bond-like interaction between the formyl C–H and the carbonyl groups. In fact, the downfield shifts are usually observed with both intra- and intermolecularly hydrogen-bonded hydroxyl and amino protons and are used frequently as a criterion to prove the presence of hydrogen bonds.

Table 6. Frequencies of C-H and C=O Stretching Vibrations of (Methoxycarbonyl)thiophenecarbaldehydes

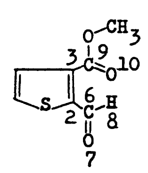
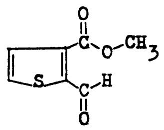
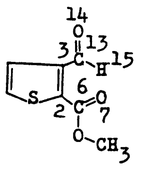
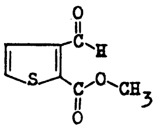
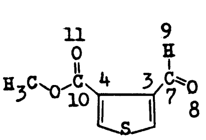
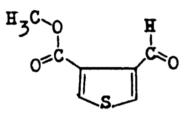
Compound	CHO						COOCH$_3$	
	$\nu_{C\text{-}H}$/cm^{-1}				$\nu_{C=H}$/cm^{-1}		$\nu_{C=H}$/cm^{-1}	
1a	2896				1673		1729	
1b	2825				1688		1731	
1c	2845	2806			1688		1731	1725$^{a)}$
3a	2904	2881			1687		1725	
3b	2891	2827			1689		1729	
3c	2845	2827	2804	2789	1704	1698$^{a)}$	1725	1735$^{a)}$

a) Shoulder peak.

Hydrogen bonds involving OH and NH groups as proton donors have been studied most frequently and most extensively by means of infrared spectroscopy.[21] Hydrogen bond formation causes a significant low frequency shift of the OH or NH stretching absorption. The hydrogen bond shift of the X-H stretching band is very often accompanied with a considerable broadening and an increase in the intensity of the band, which can be another clue to detect the presence of a hydrogen bond.[22] Thus the infrared spectra of these formyl esters were measured with the aim of proving the presence of C-H/O hydrogen bonds.

Many aldehydes have been shown by the extensive study by Pozefsky and Coggeshall[23] to have two CH stretching absorption bands near 2720 and 2820 cm^{-1}. The doubling of the absorption band has been

Table 7. Atomic and Bond Populations of the CH···O=C Hydrogen-Bonded (Most Stable) and the Next Most Stable Conformers of Methyl *o*-Formylthiophenecarboxylates

Compound	Confermer	Atom	Formal charge	Bond	Bond population
1a		C(2)	−0.1769	C(6)=O(7)	1.9697
		C(3)	−0.0785	C(9)=O(10)	1.7750
		C(6)	0.3032	C(6)-H(8)	0.8995
		O(7)	−0.2715	C(8)···O(10)	0.0049
		H(8)	0.0711		
		C(9)	0.3901		
		O(10)	−0.3873		
1a		C(2)	−0.1957	C(6)=O(7)	1.9708
		C(3)	−0.0684	C(9)=O(10)	1.7989
		C(6)	0.3077	C(6)-H(8)	0.8983
		O(7)	−0.2690	H(8)···O(10)	0.0000
		H(8)	0.0547		
		C(9)	0.3796		
		O(10)	−0.3652		
3a		C(2)	−0.1636	C(6)=O(7)	1.7752
		C(3)	−0.0951	C(13)=C(14)	1.9670
		C(6)	0.3967	C(13)-H(15)	0.9020
		O(7)	−0.3797	H(15)···O(7)	0.0047
		C(13)	0.2982		
		O(14)	−0.2791		
		H(15)	0.0624		
3a		C(2)	−0.1612	C(6)=O(7)	1.7998
		C(3)	−0.1108	C(13)=C(14)	1.9679
		C(6)	0.3863	C(13)-H(15)	0.9006
		O(7)	−0.3582	H(15)···O(7)	0.0000
		C(13)	0.3029		
		O(14)	−0.2773		
		H(15)	0.0468		
3b		C(3)	−0.1603	C(7)=O(8)	1.9550
		C(4)	−0.1113	C(10)=O(11)	1.7798
		C(7)	0.3055	C(7)-H(9)	0.9009
		O(8)	−0.2949	H(9)···O(11)	0.0067
		H(9)	0.0669		
		C(10)	0.3923		
		O(11)	−0.3833		
3b		C(3)	−0.1711	C(7)=O(8)	1.9565
		C(4)	−0.1151	C(10)=O(11)	1.7890
		C(7)	0.3099	C(7)-H(9)	0.8995
		O(8)	−0.2916	H(9)···O(11)	0.0000
		H(9)	0.0508		
		C(10)	0.3887		
		O(11)	−0.3769		

ascribed to a Fermi resonance between the CH-stretching vibration and the first overtone of the CH-deformation vibration. The higher-frequency band has been shown to have the main CH-stretching character.[24] For this reason, our attention was focused on the CH bands above 2800 cm^{-1}. In contrast to the cases of the O–H/X and N–H/X hydrogen bonds, high frequency shifts of CH-stretching absorptions have been reported with some intramolecularly hydrogen bonded CH groups. For instance, the formyl CH group of *o*-nitrobenzaldehyde has been shown to absorb at 2860 cm^{-1}, about 50 cm^{-1} higher than unsubstituted benzaldehyde (2807 cm^{-1}).[5] Similar high-frequency shifts have been observed with the formyl esters **1a**, **3a**, and **3b**, which absorb at 2896, 2904, and 2891 cm^{-1}, respectively (Table 6). The frequencies are more than 50 cm^{-1} higher than those of the other aldehydes in Table 6.

The high-frequency shift is plausible if a C–H bond can interact attractively with an electronegative group (X) without weakening itself, i.e., without a decrease in its stretching force constant (k_{CH}), because the vibrational frequency of a linear (or, when the C–H···X angle is larger than 90°) C–H/X system can be expected to become higher than the isolated C–H bond when k_{CH} remains constant.[25] The effect of the steric compression of the CH bond may also operate. However, it cannot be very significant, since the steric crowdedness around the formyl hydrogen can easily be relaxed by tilting itself towards outside the plane of the thiophene ring. 3-Methyl-2-thiophenecarbaldehyde absorbs at 2819 cm^{-1}, and the effect of possible steric compression is not reflected significantly in the frequency of its formyl absorption band, even if the steric crowdedness of a same magnitude as in the formyl esters **1a**, **3a**, and **3b** can be expected from their molecular models.

The MNDO calculations[13–15] (Table 7) helped us to gain an insight into this apparently contradictory shift of the CH-stretching bands of the *o*-formyl esters. The nonbonded H···O bond populations in the C–H/O approached conformations of the formyl esters **1a**, **3a**, and **3b** range from 4.7×10^{-3} to 6.7×10^{-3}. These populations are comparable to the total CH_3···Ph bond population (4.79×10^{-3}) in the CH_3/pi interacted conformation of 1-phenyl-2-propanol and to about half of the OH···Ph bond population (1.62×10^{-2}) of the OH/π interacted conformation of the same molecule.[26] As both the OH/π and CH/π interactions have been well characterized and supported by experimental evidence, the hydrogen-bond-like C–H/O interaction in the *o*-formyl esters becomes more realistic.

The C–H and C=O bond populations of the formyl group seemed unperturbed by the C–H/O=C interaction. In the cases of all three *o*-formyl esters, the C–H bond populations tend to increase when compared with those of the corresponding next stable conformers. However, the increase is very slight and is assumed to be negligible when the reference is extended to all the formyl esters investigated. At any rate, there is no evidence for the decrease in the C–H bond population such as is often observed with the OH and NH bonds under similar circumstances. This gave a very clear explanation for the high frequency shift of the C–H stretching vibration in the C–H/O interacted system. On the other hand, the bond population of the hydrogen-accepting carbonyl group in the methoxycarbonyl moiety was shown to decrease considerably. The decrease was not very large, but it was meaningful when the populations were compared with those of other conformations and of other isomeric formyl esters. As to the hydrogen-accepting carbonyl group of the methoxycarbonyl moiety, the atomic populations of both carbon and oxygen vary in the direction of increasing their polarity, i.e., decreasing at the originally positive carbon atom and increasing at the negative oxygen atom in the C–H/O hydrogen-bonded conformer, when compared with the other less favorable conformer. In cooperation with the change in the charge distribution in the ester carbonyl group, the hydrogen-donating C–H bond becomes more polarized without perturbing the formyl carbonyl group appreciably. Thus, the attractive interaction was shown to originate both from the delocalizative contribution revealed as the positive bond population of nonbonded H···O and from the electrostatic contribution caused by the enhanced polarization of the originally dipolar C=O and C–H groups. Both the delocalizative and electrostatic stabilzations have been known as theoretical criteria for hydrogen bonding. In conclusion, the C–H/O attractive interaction involved have been shown to be hydrogen-bond-like in their nature both by the experimental evidence and by the theoretical consequences.

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25) If we assume that the C-H group, absorbing at 2800 cm^{-1} when free, forms a linear C-H⋯X hydrogen bond keeping its stretching force constant (k_{CH}, 4.26×10^5 dyn cm) unchanged, and that the stretching force constant of the newly formed H⋯X is as large as the 1/22.4 of k_{CH}, the high frequency shift of 50 cm^{-1} could be reproduced by a simple calculation using the valence force field approximation. The authors wish to thank Mr. Tamiki Komatsuzaki for this calculation.

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