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Molecular and Electronic Structures of Thieno[3,4-*b*]thiophene-2-carboxylic Acid and Acetic Thieno[3,4-*b*]thiophene-2-carboxylic Anhydride. An AMl, MNDO, and CNDO/S Study

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AMl and MNDO methods have been used for optimizing the molecular geometry of all the possible conformations of thieno[3,4-*b*]thiophene-2-carboxylic acid (**1**), of its methyl ester (**2**) and of acetic thieno[3,4-*b*]thiophene-2-carboxylic anhydride (**3**). Both methods give comparable results for the thieno[3,4-*b*]thiophene framework but rather different bond angles for the substituent group of **3**. In any case, an equilibrium between two (**1**,**2**) or more (**3**) conformations is conceivable. Although the most stable conformations are predicted to be planar, the rotation of the substituent group implies only low energy increase (rotation barriers are calculated to be about 2 kcal mol^{-1}) which allows wide oscillations. The $\pi\rightarrow\pi^*$ electronic transitions do not differ appreciably from those of the parent thieno[3,4-*b*]thiophene molecule and are better accounted for by the conformations having remarkable rotation around the C_7–C_9 bond.

Thieno[3,4-*b*]thiophene-2-carboxylic acid (**1**), its methyl ester (**2**) and acetic thieno[3,4-*b*]thiophene-2-carboxylic anhydride (**3**) are stable derivatives[1] of the unstable thieno[3,4-*b*]thiophene. The geometry and electronic structure of this latter bicyclic compound have been previously studied at MNDO and CNDO/S level.[2] In spite of the increasing of the π system dimension, the UV absorption bands of the parent compound are still present—only slightly affected by substitution—also in the spectra of **1**—**3**, together with a new band of moderate intensity lying on the long wavelengths side (about 340 nm).[1] This band is certainly peculiar of the substituent group and probably involves oxygen(s) lone pairs.

Aim of the present study is the investigation of the electronic structures of the title compounds in order to evidence what changes occur in the electronic transitions as well as in the involved frontier MO's, with respect to those of the thieno[3,4-*b*]thiophene, consequently to the substitution of an H atom with a carboxyl or more extensive group. Moreover, we propose to investigate the role played by the molecular geometry on the electronic spectra.

Since different possible accomodations of the atoms constituting the lateral chain are conceivable, and, therefore, quite a lot of conformations can be originated, a preventive conformational analysis study has been accomplished in order to determine the relative stabilities of these conformations to select the most probable conformers.

Calculation

The geometry optimization, including all the independently variable parameters needed for geometry definition, was carried out by means of AMl method[3] since it is claimed to evaluate the "core-core" repulsion energy better than other semiempirical methods. Further optimization at MNDO level[4] was carried out too, in order to get geometries of **1**—**3** homogeneous with those previously obtained for the parent thieno[3,4-*b*]thiophene, and, on the same time, to evidence what differences, if any, characterize the molecular structures coming from the two different methods.

All the possible conformations arising from the different possible geometrical arrangements of -COOH, -$COOCH_3$, or -$COOCOCH_3$ groups of **1**—**3** were taken into account in the present study. In a first step full planarity was imposed to the molecules, then the obtained minimum energy structures were again optimized allowing free rotation to the substituent groups in order to check if loss of planarity leads to energy gain. Since MNDO is often not able to give correct geometries when rotation is considered,[5] because of its tendency to underestimation of rotation barrier energies, only AMl was used in exploring nonplanar conformations. Calculations were performed on a Vax-11-750 computer by using the AMPAC program (in which MINDO/3, MNDO, and AMl options are included) furnished by Q.C.P.E.[6]

The electronic transitions were evaluated by means of CINDO/SHIFT/UV program†[7] which allows (if wanted) inclusion of 3d atomic orbitals of S atoms. 80 monoexcited configurations were taken into account in the CI procedure. The importance of doubly excited configurations was also tested by means of the CNDUV99 program.[8]

Results and Discussion

Molecular Conformations. The most stable conformers of **1**—**3** are shown in Fig. 1. The relative stabilities resulting from our calculations are given in Table 1, where also the theoretical dipole moments are reported.

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† CNDO-SHIFT-UV program furnished by Q. C. P. E was properly modified by us to run on VAX computers and to allow calculations of the excited state dipole moments. At present a version of the same program running on IBM-PC is available too.[7b]

Table 1. Stability Order (Energies in kcal mol^{-1}) and Dipole Moments (in Debyes) of the Various Conformers

	ΔE		μ	
	MNDO	AM1	MNDO	AM1
1-A	0.367	0.0	3.21	3.37
1-ARP	9.736	5.562	5.49	5.66
1-B	0.0	0.483	2.07	2.38
1-BRP	7.874	4.828	4.76	4.95
Rotation barrier **1**-A → **1**-B=2.040 kcal mol^{-1}				
2-A	0.381	0.0	3.25	3.16
2-ARP[a)]	9.736	9.055	5.40	5.69
2-RNP	—	5.920	—	5.23
2-B	0.0	0.405	1.78	1.74
2-BRP[a)]	7.874	7.762	4.34	4.52
Rotation barrier **2**-A → **2**-B=1.803 kcal mol^{-1}				
3-A1	0.754	0.436	5.84	5.87
3-A2	3.355	0.0	2.06	2.51
3-A2RP[a)]	21.975	20.698	7.41	7.76
3-B1	0.0	0.353	4.40	4.18
3-B2	3.550	0.817	3.27	3.86
3B2RP[a)]	18.861	16.991	7.01	7.25
Rotation barrier **3**-A2 → **3**-B2=2.41 kcal mol^{-1}				

a) Pseudo minimum. P=Planar, NP=Nonplanar.

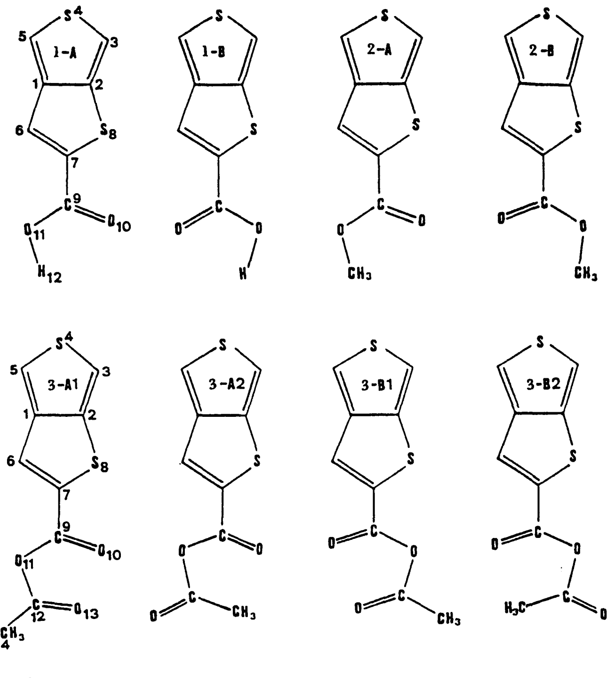
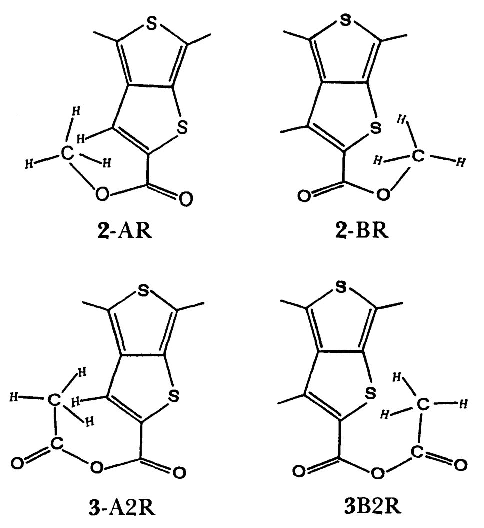


Fig. 1. Numbering system and molecular structure of the most stable conformations of **1**—**3**.

Additionally to the conformations of Fig. 1, we took into account also the less probable structures in which the H, CH_3, or $COCH_3$ groups are oriented towards the bicyclic framework, i.e. having $\omega_{10\text{-}9\text{-}11\text{-}12}=180°$. They will be indicated as **1**-AR, **2**-BR, **2**-AR, and so on. **1**-AR and **1**-BR minimum energy geometries retain their planarity after optimization but are less stable than **1**-A and **1**-B by 5.56 and 4.83 kcal mol^{-1}, respectively. The corresponding planar conformations of **2** and **3**



2-AR **2**-BR

3-A2R **3**B2R

Fig. 2. Pseudo minima found when S_8 or the H bonded to C_6 bisects the bond angle of the methyl out-of-plane H atoms.

(**2**-ARP, **2**-BRP, **3**-A2RP, and **3**-B2RP) reach pseudo minima when the two out of plane H atoms of the CH_3 group are arranged as shown in Fig. 2. In such a situation, owing to the interaction with the H atom bonded to C_6 or with the S_8 electronic cloud, any rotation of the methyl group causes energy increasing which prevents the displacement towards the most stable structures **2**-A, **2**-B, **3**-A2, and **3**-B2 (a similar pseudo minimum was previously noticed in studying the molecular structures of methoxy derivatives of heptalenediones.[9)] Since **2**-ARP, **2**-BRP, **3**-A2RP, and **3**-B2RP forms are by far less stable than **2**-A, **2**-B, **3**-A2, and **3**-B2, no detail about their geometrical parameters is reported here. When the above cited pseudo minima were avoided a different behavior of **2** and **3** was found. In particular, both **2**-AR and **2**-BR converge towards a nonplanar single minimum energy structure (indicated as **2**-RNP in Table 1) in which the CH_3 group is still oriented towards the thieno[3,4-*b*]thiophene framework but has the whole $COOCH_3$ group rotated by about 80° around the C_7–C_9 bond.

Differently from **3**-A2R and **3**-B2R, the conformers **3**-A1R and **3**-B1R show no minimum and after optimization, come back to **3**-A1 and **3**-B1 respectively. **3**-A2 and **3**-B2 are all planar conformations whilst **3**-A1 and **3**-B1 are not, because of repulsion between O_{10} and O_{13} which causes rotation of about 20° around to the C_9–O_{11} and O_{11}–C_{12} bond; however, the energy difference between the planar and nonplanar structures is very low: $\simeq$0.3 kcal mol^{-1}. These results lead to the conclusion that the $OCOCH_3$ group in **3** can widely oscillate. Although null or negligible rotation around the C_7–C_9 bond is predicted for the most probable conformations of **1**—**3** the calculated torsion barriers are not excessively high and the related potential well is rather flattened (in **1** and **2** a rotation of 45° of the substituent group implies an energy increase lower

Table 2. Optimized Molecular Geometry of Thieno[3,4-*b*]thiophene Framework of **1**-A Conformer

	AM1	MNDO	MNDO[a)]		AM1[b)]	MNDO	MNDO[a)]
r_{1-2}	1.468	1.475	1.478	δ_{5-1-2}	111.8	111.2	110.8
r_{2-3}	1.362	1.370	1.364	δ_{1-2-3}	112.2	111.8	112.6
r_{3-4}	1.680	1.682	1.690	δ_{2-3-4}	109.9	110.7	110.4
r_{4-5}	1.673	1.677	1.689	δ_{3-4-5}	95.9	95.3	94.9
r_{5-1}	1.367	1.376	1.371	δ_{4-5-1}	110.2	110.9	111.3
r_{1-6}	1.442	1.456	1.457	δ_{6-1-2}	110.7	110.4	110.3
r_{6-7}	1.366	1.376	1.365	δ_{1-6-7}	111.7	111.5	111.1
r_{7-8}	1.712	1.711	1.702	δ_{6-7-8}	113.4	113.3	114.6
r_{2-8}	1.677	1.674	1.687	δ_{7-8-2}	93.4	94.1	93.3
r_{C-H}	1.090	1.081	1.082	δ_{8-2-1}	110.8	110.7	110.7

a) Isolated molecule. The geometry of this framework does not change significantly in the other conformers. b) $\delta_{H-C_3-C_2}=129.5$; $\delta_{H-C_5-C_1}=128.9$; $\delta_{H-C_6-C_1}=123.3$.

Table 3. Optimized Geometries of the Substituent Groups in the Studied Molecules

	1-A		**1**-B		**2**-A		**2**-B	
	AM1	MNDO	AM1	MNDO	AM1	MNDO	AM1	MNDO
r_{7-9}	1.453	1.482	1.454	1.481	1.456	1.484	1.457	1.484
r_{9-10}	1.235	1.232	1.238	1.233	1.233	1.229	1.236	1.230
r_{9-11}	1.369	1.360	1.365	1.358	1.374	1.363	1.370	1.360
r_{11-12}	0.972	0.949	0.972	0.950	1.430	1.407	1.431	1.407
$r_{CH(methyl)}$	—	—	—	—	1.117	1.108[a)]	1.117	1.108[a)]
δ_{6-7-9}	125.6	127.9	122.9	124.9	125.9	128.2	122.7	124.8
δ_{7-9-10}	129.9	126.4	127.4	126.0	129.4	126.1	126.9	125.6
δ_{7-9-11}	114.0	115.3	116.4	115.5	112.9	114.0	115.1	114.3
$\delta_{9-11-12}$	109.0	115.2	108.9	115.3	116.1	125.2	116.1	125.2
$\delta_{HCH(methyl)}$	—	—	—	—	107.8	110.3	107.8	110.3

	3-A1		**3**-A2		**3**-B1		**3**-B2	
	AM1	MNDO	AM1	MNDO	AM1	MNDO	AM1	MNDO
r_{7-9}	1.455	1.485	1.455	1.482	1.457	1.484	1.457	1.483
r_{9-10}	1.226	1.223	1.230	1.226	1.228	1.224	1.233	1.227
r_{9-11}	1.390	1.374	1.378	1.366	1.384	1.371	1.372	1.364
r_{11-12}	1.387	1.374	1.393	1.379	1.388	1.374	1.396	1.380
$r_{CH(methyl)}$	1.117	1.108[a)]	1.118	1.108[a)]	1.117	1.108[a)]	1.118	1.108[a)]
r_{12-13}	1.224	1.221	1.229	1.226	1.223	1.222	1.228	1.225
r_{12-14}	1.488	1.525	1.482	1.523	1.488	1.525	1.482	1.523
δ_{6-7-9}	126.0	128.4	125.7	128.2	122.6	124.6	122.4	124.5
δ_{7-9-10}	130.1	126.4	129.3	126.5	127.5	126.1	126.7	126.0
δ_{7-9-11}	112.3	113.3	111.7	113.4	114.5	113.4	114.1	113.7
$\delta_{9-11-12}$	121.5	131.5	124.4	133.9	121.7	131.8	124.2	133.6
$\delta_{HCH(methyl)}$	109.5	110.6	109.8	110.8	109.5	110.6	109.8	110.8
$\delta_{11-12-13}$	118.5	120.8	109.6	111.5	118.7	120.7	109.6	111.5
$\delta_{11-12-14}$	111.6	112.3	122.4	123.8	111.4	112.3	122.4	123.9
$\omega_{10-9-7-8}$	1.5	—	0.2	—	−178.6	—	180.0	—
$\omega_{12-11-9-7}$	−156.5	—	179.9	—	157.0	—	180.0	—
$\omega_{13-12-11-9}$	21.4	—	178.7	—	−19.2	—	180.0	—

a) This bond length was not optimized at MNDO level. MNDO geometries refer to all planar conformations (see text).

than 1 kcal mol^{-1}) so that wide oscillations around this bond are also possible. Let we now analyze more carefully the details of AM1 and MNDO geometries of the bicyclic framework and of the substituent groups, reported in Tables 2 and 3, respectively.

A first remark to point out is that, independently of the adopted method, the geometry of the thieno[3,4-*b*]thiophene framework is practically the same calculated for the parent compound and it does not change significantly on changing the attached group. As it can be seen by comparing the geometrical data of **1**-A, reported in Table 2, the ring bond lengths differ by about 0.01 Å and bond angles by about one degree on passing from AM1 to MNDO or from the substituted to the unsubstituted molecule. These findings are noticed in compounds **2** and **3** too. More important differences between AM1 and MNDO geometries occur in the -COOR and, mainly, in the -COOCOCH$_3$ framework (see Table 3). In particular, the C$_7$-C$_9$ bond length, in all the examined compounds, and the C$_{12}$-C$_{14}$ bond length in **3** are predicted by AM1 about 0.03 Å shorter than the MNDO ones, whilst $r_{\text{O-CH}_3}$ in **2**-A and **2**-B is calculated by AM1 about 0.02 Å longer than that calculated by MNDO.

In all conformers of A type $\delta_{6\text{-}7\text{-}9}$ is 3—4 degrees larger than in the conformers of B type: being $\delta_{6\text{-}7\text{-}9}$ value practically constant, the substituent group is bent towards the right more than it is in B type conformers. This could be due, at least partially, to a lower repulsion between S$_8$ and oxygen with respect to that between C$_6$-H and oxygen owing to a greater interatomic distance in the former case, deriving from the large C$_7$-S$_8$ bond length in comparison with C$_6$=C$_7$ double bond length. Moreover the MNDO values concerning $\delta_{9\text{-}11\text{-}12}$ are, in general, from six to ten degrees larger than AM1 ones. These large angle differences are to be ascribed to the overestimation of "core-core" repulsion by MNDO with respect to AM1 method. As a consequence, the two methods lead to different final stability order, at least for the most probable conformations. So MNDO predicts structures **1**-B, **2**-B, and **3**-B1 to be the most stable ones, in contrast with AM1, which indicates **1**-A, **2**-A, and **3**-A2 as the most stable conformers. Indeed, apart from the question about which of them is the most stable, the ΔE between structures **1**-A and **1**-B and between **2**-A and **2**-B, both at MNDO and AM1 level, is less than 0.5 kcal mol^{-1}, whilst the ΔE among **3**-A2, **3**-B1, **3**-A1, and **3**-B2, at AM1 level, are less than, or, at the most, equal to 1 kcal mol^{-1}. On this ground an equilibrium between these structures is conceivable.

At present, at best of our knowledge, no experimental support is available in favor of one or another conformation. Unfortunately, the calculated electronic spectra of the above conformers are not sufficiently different from each other. However we note that the calculated dipole moments of the cited conformations are rather unlike one another, therefore an important contribution to the problem could be achieved from their measurement.

Electronic Spectra. As previously pointed out for thieno[3,4-*b*]thiophene,[2)] the contribution of 3d orbitals of sulfur atoms to the orbitals involved in the low energy electronic transitions is very low.

The molecular orbitals involved in the electronic transitions responsible of the UV absorption maxima of **1**—**3** are chiefly the two highest occupied (π_1 and π_2) and the two lowest vacant (π_1* and π_2*) together with the *n* ones. In **1** and **2** the n orbital is mainly localized on O$_{10}$, whilst in **3** we have two n orbitals whose highest coefficients are located mainly on O$_{10}$ and O$_{13}$, respectively.

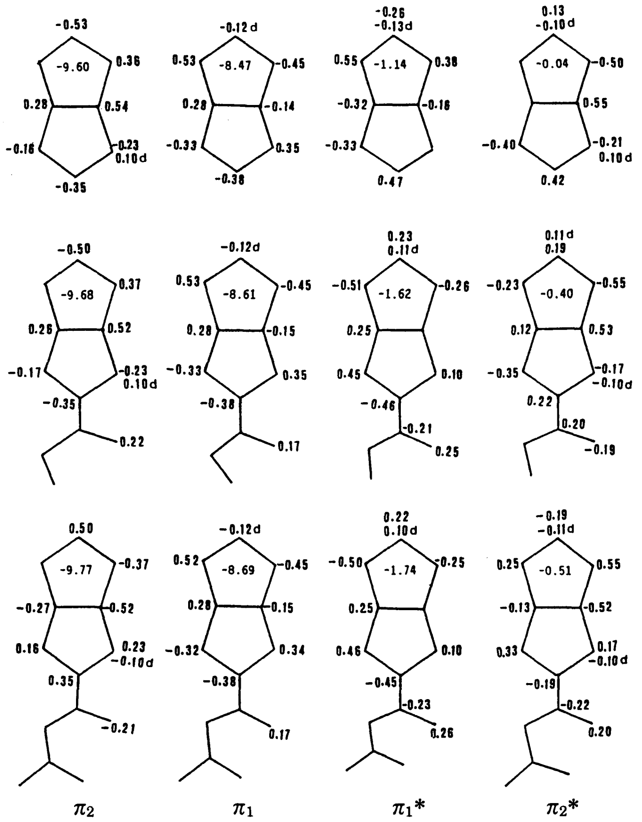


Fig. 3. Coefficient distribution of the two highest occupied (HOMO and NHOMO) and the two lowest unoccupied (LUMO and NLUMO) MO's of thieno[3,4-*b*]thiophene and its derivatives **1** and **3**. The figures inside the rings are the orbital energies (in eV). The n-type orbitals were calculated at −11.32 eV in **1**-A, at −11.23 eV in **2**-A, and at −11.06 and −11.68 eV in **3**-A2.

Figure 3 shows the coefficient distribution of π_1, π_2, π_1*, and π_2* of **1** and **3** (the coefficient distribution of the frontier MO's of **2** is not reported because it is practically coincident with that of the MO's of **1**). In the same figure also the corresponding MO's of the thieno[3,4-*b*]thiophene are reported for comparison. It appears clearly that the coefficient distribution on the bicyclic framework is practically equal in the parent and in the derivative compounds, although nonnegligible coefficients are found also on O$_{10}$ (π_1 and π_2) and on the C$_9$=O$_{10}$ fragment (π_1* and π_2*). Owing to the fact that these MO's in **3** do not span appreciably the extreme COCH$_3$ framework (which is the most rotated with respect to the molecular plane), the electronic transitions calculated by adopting the minimum energy conformations (nonplanar) or the planar ones, are practically coincident (differences are limited to 1 or 2 nm). Similarly, no appreciable difference exists between the calculated transitions of A and B type structures.

The charge densities on the atoms of the bicyclic framework mantain the same order noted in the parent compound,[2)] so that also in **1**—**3** the C atoms in α position with respect to S are once again the most negatively charged.

Table 4. Electronic Transitions (eV) of **1**—**3** in Their Minimum Energy Conformation (Geometries from AMl method).

E	λ	f	Pol.[a)]	Nature	Exp.[b)]		
					λ	E	log ε
Thieno[3,4-*b*]thiophene[c)]							
4.43(4.53)	280	0.32(0.35)	27(31)	$\pi_1\to\pi_1^*$	297	4.18	3.73
					276	4.50	3.56
4.65(4.82)	266	0.02(0.02)	102(74)	$\pi_1\to\pi_2^*$; $\pi_2\to\pi_1^*$	266	4.66	3.56
					257	4.82	3.53
5.39(5.41)	230	0.51(0.49)	97(99)	$\pi_1\to\pi_2^*$; $\pi_2\to\pi_1^*$	235	5.27	4.23
5.54(5.71)	224	0	—				
5.98(6.06)	207	0.05(0.09)	49(73)	$\pi_1\to\pi_3^*$; $\pi_2\to\pi_2^*$			
Thieno[3,4-*b*]thiophene-2-carboxylic acid[c)] (**1**-A)							
3.60(3.58)	344	0	—	$n\to\pi^*$	336	3.69	3.64
4.18(4.22)	296	0.35(0.38)	39(43)	$\pi_1\to\pi_1^*$	292	4.24	4.18
					283	4.38	4.20
4.59(4.75)	270	0.23(0.29)	107(74)	$\pi_2\to\pi_1^*$; $\pi_1\to\pi_2^*$	260	4.77	4.07
					255_{sh}	4.86	4.06
5.07(5.12)	244	0.52(0.42)	104(70)	$\pi_1\to\pi_2^*$; $\pi_2\to\pi_1^*$	232	5.34	3.74
5.46(5.60)	227	0	—	$\sigma,n\to\pi^*$			
5.76(5.85)	215	0.02(0.09)	86(81)	$\pi_1\to\pi_3^*$; $\pi_2\to\pi_2^*$	226	5.50	3.73
5.98(6.09)	207	0.04(0.10)	94(101)	$\pi_3\to\pi_1^*$; $\pi_2\to\pi_2^*$			
Thieno[3,4-*b*]thiophene-2-carboxylic ester[d)] (**2**-A)							
3.58(4.01)	346	$10^{-5}(10^{-4})$	—	$n\to\pi^*$	340	3.65	3.62
4.20(4.46)	295	0.35(0.35)	141	$\pi_1\to\pi_1^*$	293	4.23	4.23
					284	4.36	4.22
4.59(4.64)	270	0.22(0.04)	73	$\pi_2\to\pi_1^*$; $\pi_1\to\pi_2^*$	262	4.74	4.02
					256_{sh}	4.84	4.00
5.07(5.33)	244	0.53(0.57)	104	$\pi_1\to\pi_2^*$; $\pi_2\to\pi_1^*$	234	5.31	3.66
5.51(5.50)	225	0	—	$\sigma,n\to\pi^*$			
5.77(5.92)	215	0.02(0.03)	83	$\pi_1\to\pi_3^*$; $\pi_2\to\pi_2^*$			
5.99(5.98)	207	0.10(0)	92	$\pi_3\to\pi_1^*$; $\pi_2\to\pi_2^*$			
Acetic thieno[3,4-*b*]thiophene-2-carboxylic anhydride (**3**-A2)							
3.74	332	0	—	$n\to\pi^*$	343	361	3.58
4.03	308	10^{-3}	—	$n\to\pi^*$			
4.18	297	0.35	140	$\pi_1\to\pi_1^*$	292	4.24	4.22
					284_{sh}	4.36	4.14
4.60	270	0.24	107	$\pi_2\to\pi_1^*$; $\pi_1\to\pi_2^*$	260	4.78	3.98
5.06	245	0.52	114	$\pi_1\to\pi_2^*$; $\pi_2\to\pi_1^*$	238_{sh}	5.21	3.69
5.55	224	0	—	$\sigma,n\to\pi^*$			
5.75	215	0.02	86	$\pi_2\to\pi_2^*$; $\pi_1\to\pi_4^*$			
5.98	207	0.20	75	$\pi_3\to\pi_1^*$; $\pi_2\to\pi_2^*$			

a) Angle between the transition moment vector and the short molecular axis. b) Ref. 1 (95% ethanol). c) Values in parentheses are those obtained without d orbitals inclusion. d) Values in parentheses refer to the conformation rotated by 90° around C_7-C_9.

The CNDO/S results obtained for the most stable conformers (AMl geometries) are collected in Table 4, together with those of thieno[3,4-*b*]thiophene, for which the optimized geometry coming from AMl method was adopted too. Here also the literature experimental absorption maxima are reported. These latter were recorded in 95% EtOH solution. According to Skancke[10)] the vapor phase values of thieno[3,4-*b*]thiophene would be roughly 0.08 eV higher than the solution ones. A similar correction could be accepted also for **1**—**3**.

By comparing the experimental absorption maxima of thieno[3,4-*b*]thiophene and those of **1**—**3** we observe two noteworthy features: i) The maxima centered at 297 and 266 nm in the spectrum of the parent compound shift by 4—5 nm towards the blue after substitution; ii) the two maxima recorded at 276 and 257 nm in the thieno[3,4-*b*]thiophene spectrum, where they are equidistant from the band at 266 nm, show to be differently affected by substitution: The former shifts towards the red and is found in the range of 280 nm, the latter remains unchanged in **1**—**2** and is absent in **3**.

Theory predicts that the lowest energy transition of **1** and **2** and the lowest two transitions of **3** are $n\to\pi^*$ in nature: they are responsible of the absorption band observed in the range of 3.6 eV.

Owing to the slight changes noted in the frontier orbitals of the title molecules, also the lowest energy $\pi\to\pi^*$ transitions undergo negligible changes with

Table. 5. Electronic Transitions (eV) of the Title Compounds after Inclusion of Doubly Excited Configurations

E	λ	f	$\log \varepsilon$	%DEC[a)]	E	λ	f	$\log \varepsilon$	%DEC[a)]
	Thieno[3,4-*b*]thiophene						**1**		
4.43	280	0.02	2.96	18	4.09	303	0.11	3.78	7
4.63	268	0.16	3.94	4	4.54	273	0.12	3.81	10
5.18	239	0.02	3.13	37	4.83*	256	0	—	—
5.70	218	0.27	4.16	9	5.04	246	0.17	3.96	18
6.37	195	10^{-3}	1.84	8	5.46	227	0.17	3.96	25
					6.00	207	$7\cdot10^{-3}$	2.55	6
		2					**3**		
4.08	304	0.10	3.74	8	4.08	304	0.15	3.91	5
4.54	273	0.13	3.85	11	4.59	270	0.08	3.63	12
4.83*	257	0	—	—	5.01*	248	0	—	—
5.05	246	0.16	3.95	18	5.03	247	0.24	4.12	11
5.44	228	0.21	4.06	22	5.19*	239	10^{-4}	0.91	—
6.02	206	0.01	2.70	—	5.48	226	0.10	3.72	30
					5.98	207	$6\cdot10^{-3}$	2.52	6

a) Total percentage of doubly excited configurations. Values marked with * refer to n→π* transitions.

respect to those of the parent compound. So the band at 4.2 eV is mainly due to the $\pi_1 \rightarrow \pi_1^*$, HOMO→LUMO transition, whilst the two bands recorded at 4.7 and 5.3 eV originate from HOMO→NLUMO and NHOMO→LUMO transitions. The oscillator strength of the transition calculated at 4.6 eV is strongly enhanced by substitution but it becomes gradually weaker as the substituent goes away from planarity.

The two experimental maxima centered at 284 nm and at about 255 nm, corresponding to the maxima at 276 and 257 nm of thieno[3,4-*b*]thiophene, are not supported by calculations: this occurred also in the parent compound, where they lie in a wavelengths range affected by a vibrational progression and were assigned to vibrational modes. Although in **1**—**3** they are no more equidistant from the band recorded at 266 nm, we think they originate once again from molecular vibrations.

The two lowest virtual orbitals of **1**—**3** are stabilized by substitution more than the two highest occupied ones, so that the calculated $\pi \rightarrow \pi^*$ transitions involving them are calculated 10—15 nm shifted towards the red with respect to those of thieno[3,4-*b*]thiophene. This result, seems contrasting with the weak blue shift appearing in the experimental findings, even if it is in line with the red shift observed on passing from the spectrum of benzene to that of the benzoic acid.[11)] However, the eletronic transition energies of **1**—**3** shift towards the blue when remarkable rotation around C_7-C_9 is considered (see values in parentheses for **2** in Table 4). This behavior, together with the fact that the rotation barrier of the carboxyl group (calculated by the same method[2)]) in the benzoic acid is ≃1 kcal mol^{-1} higher than in **1**, suggest that contributions from conformers highly rotated around C_7-C_9 are important in the electronic structure description of the title compounds.

Calculations carried out by using CNDUV/99 program,[8)] in order to test the importance of doubly excited configurations, are reported in Table 5. Apart from an overestimation of the n→π* transition(s) (a peculiarity of this program), also these last results support the above assignments and conclusions as regards the $\pi \rightarrow \pi^*$ transitions. Double excitations are present in percentages comparable with those noticed in the parent molecule and the highest total value was found for the transitions lying at ≃5—5.4 eV.

Conclusion

The results of the present study indicate that the most stable conformations of **1**—**3** have the substituent group coplanar to the bicyclic framework. The low energy difference between the most stable conformers (two in **1**, **2**, four in **3**) suggests the possibility of an equilibrium among them; moreover the rather flattened potential well when rotation around C_7-C_9 is considered allows a wide out of plane oscillation of the substituent group.

The frontier molecular orbitals of **1**—**3** show a coefficient distribution similar to that observed for thieno[3,4-*b*]thiophene with a weak extension on C_9 and O_{10}. The absorption band on the long wavelengths side originates from n→π* transitions. The two maxima lying in the range of 280 and 250 nm are probably to be assigned to vibrational modes. The slight blue shift (4—5 nm) shown by the lowest energy bands on passing from the parent compound to its derivatives can be accounted for if a remarkably contribution from the conformers with high rotation around the C_7-C_9 bond is assumed.

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