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Electronic Structures of Thianthrene, Phenothiazine, and Related Heterocyclic Compounds

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Systematic studies were made on thianthrene, phenoxathiin, diphenylene dioxide, phenothiazine, and phenoxazine for the correlation between the folded structure and electronic spectra in terms of the semiempirical SCF–MO–CI method. The calculated results are in good agreement with the experimental results, the folded structure being prominent in the sulfur-containing molecules. The dihedral angle dependency of the all valence-electronic energy and ionization potential was also studied by the extended Hückel method.

Electronic structures of the heterocyclic compounds thianthrene, phenoxathiin, diphenylene dioxide, phenothiazine, and phenoxazine are of interest since the data on dipole moment[1] and X-ray analysis[2] indicate that these compounds, sulfur-containing ones in particular, are of non-planar spacial configurations folded about the central axis joining the heteroatoms. Several molecular orbital studies have been undertaken in order to survey the correlations between the extent of the folded structure and various physico-chemical properties. As regards the Hückel MO studies, the best integral values for the thianthrene analogs were studied by Kuboyama referring to the energies of the charge-transfer bands.[3] The value of the dihedral angle of thianthrene was predicted by Chandra in terms of the

1) a) K. Higasi, *Sci. Papers Inst. Phys. Chem. Res.* (Tokyo), **38**, 331 (1941); b) N. J. Leonard and L. E. Sutton, *J. Amer. Chem. Soc.*, **70**, 1564 (1948); c) H. Musso, *Chem. Ber.*, **92**, 2881 (1959); d) H. Lumbroso and G. Montando, *Bull. Soc. Chim. France*, **9**, 2119 (1964).

2) a) H. Lyton and E. G. Cox, *J. Chem. Soc.*, 488 (1956); b) I. Rowe and B. Post, *Acta Crystallogr.*, **11**, 372 (1958); c) S. Hosoya, *ibid.*, **16**, 310 (1963); *ibid.*, **20**, 429 (1966); d) J. D. Bell, J. F. Blount, O. V. Briscol, and H. C. Freeman, *Chem. Commun.*, 1656 (1968).

3) A. Kuboyama, *J. Amer. Chem. Soc.*, **86**, 164 (1964).

electronic and strain energies.[4] The spacial configuration and electronic properties of phenothiazine were studied by Malrieu and Pullman,[5] and by Bloor *et al.*[6] from a biological viewpoint. With respect to the SCF MO study, Wratten and Ali performed a P–P–P type calculation on the neutral molecule and cation radical of diphenylene dioxide by making adequate allowance for non-planarity.[7] An analogous calculation was applied by the present author to a series of the related heterocyclic compounds.[8] It seems, however, that no systematic calculation has been published concerning at least the dihedral angle dependence of the electronic spectra and also the hybridization state of the heteroatoms.

The calculations in this paper have been performed in order to supply such deficient data.

Calculation Method

In the semiempirical SCF MO method (P–P–P approximation)[9] the valence-state ionization potential (I) and electron affinity (A) of the π-orbitals are taken as follows referring to the data given by Hinze and Jaffé.[10]

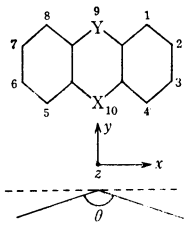
I(=C–) 11.16 eV, I(–O–) 32.90, I(–S–) 23.59, I(–$\overset{|}{\text{N}}$–) 26.70

A(=C–) 0.03 eV, A(–O–) 11.37, A(–S–) 10.54, A(–$\overset{|}{\text{N}}$–) 9.26

The two-center repulsion integral is obtained by the Nishimoto-Mataga formula.[11] For the sake of comparison the core-resonance integral is evaluated by the following two methods. In method I, the integral β_{rs} is evaluated for all atomic pairs by the equation $\beta_{rs}=-\frac{1}{2}S_{rs}(I_r+I_s)$, where the overlap integral S_{rs} is calculated on the basis of the Slater type atomic orbitals. In method II, β_{rs} is evaluated for neighbouring pairs by the variable β procedure,[12] where the parametrization is taken as follows.

$$\beta_{C-C} = -0.51P_{C-C} - 1.84$$
$$\beta_{C-O} = -0.56P_{C-O} - 2.20$$
$$\beta_{C-N} = -0.53P_{C-N} - 2.02$$
$$\beta_{C-S} = -0.33P_{C-S} - 1.80$$

Here, P_{rs} corresponds to the usual π-bond order, and to allow for non-planarity the β_{C-X} (X=heteroatom) is corrected by the equation $\beta_{C-X}(\alpha)=\beta_{C-X}(O)\cos\alpha$, where the $\beta_{C-X}(O)$ is the value for the planar structure, and the value of α is the distortion angle from planarity. In both methods all singly excited configurations are allowed to interact.



X=Y=S (I)
X=O, Y=S (II)
X=Y=O (III)
X=S, Y=NH (IV)
X=O, Y=NH (V)

Fig. 1. Molecular geometry and structural formula

TABLE 1. DIHEDRAL ANGLE DEPENDENCE OF THE CALCULATED π-π^* TRANSITION ASSIGNED TO THE LOWEST OBSERVED BAND

θ[a]	method I		method II	
	ΔE_S(eV)[b]	f[c]	ΔE_S(eV)	f
a) Thianthrene (I)				
180°	2.487	0.600	3.815	0.163
170°	2.501	0.594	3.819	0.160
160°	2.539	0.579	3.830	0.153
150°	2.608	0.552	3.849	0.142
140°	2.716	0.510	3.875	0.127
130°	2.866	0.453	3.908	0.110
120°	3.086	0.379	3.948	0.091
b) Phenoxathiin (II)				
180°	3.202	0.529	3.787	0.172
170°	3.217	0.520	3.791	0.169
160°	3.261	0.495	3.803	0.162
150°	3.339	0.452	3.822	0.150
140°	3.459	0.391	3.849	0.134
130°	3.626	0.312	3.884	0.116
120°	3.858	0.212	3.925	0.096
c) Diphenylene Dioxide (III)				
180°	4.173	0.304	3.750	0.188
170°	4.187	0.297	3.754	0.186
160°	4.232	0.279	3.766	0.178
150°	4.308	0.249	3.786	0.165
140°	4.419	0.210	3.814	0.149
130°	4.560	0.163	3.850	0.129
120°	4.709	0.116	3.893	0.108
d) Phenothiazine (IV)				
180°	2.881	0.562	3.587	0.222
170°	2.895	0.555	3.591	0.219
160°	2.934	0.535	3.602	0.211
150°	3.003	0.502	3.621	0.198
140°	3.110	0.454	3.646	0.180
130°	3.260	0.394	3.679	0.159
120°	3.471	0.323	3.717	0.136
e) Phenoxazine (V)				
180°	3.729	0.397	3.540	0.250
170°	3.743	0.390	3.543	0.247
160°	3.785	0.370	3.555	0.238
150°	3.858	0.336	3.574	0.224
140°	3.967	0.289	3.600	0.205
130°	4.117	0.228	3.634	0.182
120°	4.309	0.147	3.674	0.157

a) Dihedral angle between the lateral benzene planes
b) Singlet π-π^* transition energy calculated with CI
c) Oscillator strength

4) A. K. Chandra, *Tetrahedron*, **19**, 471 (1963).
5) J. P. Malrieu and B. Pullman, *Theor. Chim. Acta*, **2**, 293 (1964).
6) J. E. Bloor, B. R. Gilson, R. J. Haas, and C. L. Zirkle, *J. Med. Chem.*, **13**, 922 (1970).
7) R. J. Wratten and M. A. Ali, *Mol. Phys.*, **13**, 233 (1967).
8) M. Kamiya, *Bull. Chem. Soc. Japan*, **43**, 3929 (1970).
9) R. Pariser and R. G. Parr, *J. Chem. Phys.*, **21**, 466, 767 (1953); J. A. Pople, *Trans. Faraday Soc.*, **49**, 1375 (1953).
10) J. Hinze and H. H. Jaffé, *J. Amer. Chem. Soc.*, **84**, 540 (1962).
11) K. Nishimoto and N. Mataga, *Z. Physik. Chem.*, **12**, 335 (1957).
12) K. Nishimoto and L. S. Forster, *Theor. Chim. Acta*, **4**, 155 (1966).

TABLE 2. COMPARISON BETWEEN THE EXPERIMENTAL AND THEORETICAL SPECTRA AROUND THE OPTIMUM DIHEDRAL ANGLE VALUES

a) Thianthrene (I)

Calcd.	$\theta=130°$ method I		$\theta=130°$ method II		$\theta=120°$ method I		$\theta=120°$ method II		Obsd.[b] ΔE_{max}(eV) ($\log\varepsilon_{max}$)	
	ΔE_S(eV)	f	ΔE_S(eV)	f	ΔE_S(eV)	f	ΔE_S(eV)	f		
	2.004	0.000	3.814	0.000	2.441	0.000	3.880	0.000		
	2.866	0.453	3.908	0.110	3.086	0.379	3.948	0.091	x }	4.13 (2.9)
	3.534	0.055	4.097	0.009	3.593	0.072	4.117	0.012	z }	
	4.234	0.283	4.908	0.133	4.359	0.272	4.908	0.123	y	4.81 (4.6)
	5.073	1.518	5.011	0.938	5.158	1.111	5.008	0.816	x	5.10
	5.230	0.000	5.414	0.059	5.471	0.000	5.397	0.076	z	
	5.675	0.001	5.702	0.000	5.620	0.036	5.698	0.000		
	5.709	0.037	5.783	0.090	5.786	0.000	5.771	0.076	y	
	5.748	0.000	6.112	0.279	5.828	0.000	6.065	0.245	x	5.93
	6.133	0.083	6.242	0.235	6.065	0.092	6.201	0.170	y	
	ΔE_T(eV)[a] 1.100		ΔE_T(eV) 1.838		ΔE_T(eV) 1.446		ΔE_T(eV) 1.859			

b) Phenoxathiin (II)

Calcd.	$\theta=130°$ method I		$\theta=130°$ method II		$\theta=120°$ method I		$\theta=120°$ method II		Obsd. ΔE_{max} (eV) ($\log\varepsilon_{max}$)	
	ΔE_S(eV)	f	ΔE_S(eV)	f	ΔE_S(eV)	f	ΔE_S(eV)	f		
	3.234	0.170	3.755	0.002	3.598	0.203	3.825	0.003	x	
	3.626	0.312	3.884	0.116	3.858	0.212	3.925	0.096	x }	4.20 (3.60)
	3.853	0.085	4.103	0.010	3.954	0.088	4.121	0.012	y }	
	4.926	0.191	5.008	0.122	4.992	0.180	5.007	0.114	y	5.14 (4.50)
	5.428	0.626	5.045	1.021	5.455	0.281	5.043	0.889	x	5.21 (4.50)
	5.835	0.078	5.497	0.052	5.741	0.073	5.477	0.065	y	5.64
	6.062	0.062	5.728	0.003	6.170	0.004	5.725	0.003	x	
	6.219	0.005	5.810	0.070	6.214	0.479	5.797	0.058	y	
	6.306	0.252	6.189	0.281	6.367	0.478	6.140	0.252	x	
	6.457	0.117	6.298	0.309	6.412	0.097	6.255	0.211	y	
	ΔE_T(eV) 1.883		ΔE_T(eV) 1.795		ΔE_T(eV) 2.141		ΔE (eV) 1.820			

c) Diphenylene Dioxide (III)

Calcd.	$\theta=180°$ method II		$\theta=180°$ method I		$\theta=170°$ method II		$\theta=170°$ method I		Obsd. ΔE_{max}(eV) ($\log\varepsilon_{max}$)	
	ΔE_S(eV)	f	ΔE_S(eV)	f	ΔE_S(eV)	f	ΔE_S(eV)	f		
	3.508	—	3.861	—	3.515	0.000	3.885	0.000		
	3.750	0.188	4.173	0.304	3.754	0.186	4.187	0.297	x	4.13
	4.079	—	4.500	—	4.080	0.000	4.505	0.001	z	4.29 (3.87)
	5.074	1.498	5.460	0.220	5.074	1.481	5.467	0.217	y	5.44 (4.73)
	5.109	0.136	5.631	1.351	5.109	0.135	5.635	1.323	x	5.58 (4.64)
	5.632	—	6.154	—	5.630	0.002	6.149	0.002	z	6.11
	5.749	—	6.372	—	5.751	0.000	6.376	0.000		
	5.854	0.078	6.472	0.114	5.852	0.077	6.467	0.110	y	
	6.374	0.292	6.784	—	6.370	0.290	6.796	0.000		
	6.425	0.834	6.943	0.697	6.423	0.814	6.934	0.484	x	
	ΔE_T(eV) 1.668		ΔE_T(eV) 2.298		ΔE_T(eV) 1.671		ΔE_T(eV) 2.312			

d) Phenothiazine (IV)

Calcd.	$\theta=140°$ method I		$\theta=140°$ method II		$\theta=130°$ method I		$\theta=130°$ method II			Obsd. ΔE_{max} (eV) ($\log\varepsilon_{max}$)
	ΔE_S(eV)	f	ΔE_S(eV)	f	ΔE_S(eV)	f	ΔE_S(eV)	f		
	2.352	0.025	3.303	0.042	2.632	0.026	3.354	0.042	x	
	3.110	0.454	3.646	0.180	3.260	0.394	3.679	0.159	x	3.87 (3.64)
	3.666	0.062	3.934	0.016	3.713	0.070	3.946	0.019	y	
	4.505	0.244	4.804	0.154	4.569	0.242	4.800	0.146	y	4.89 (4.65)
	5.133	1.347	4.870	1.042	5.183	1.074	4.863	0.922	x	
	5.534	0.024	5.356	0.041	5.693	0.019	5.336	0.057	y	
	5.809	0.035	5.611	0.037	5.740	0.040	5.607	0.038	x	
	5.897	0.051	5.749	0.089	5.935	0.035	5.738	0.082	y	
	5.952	0.006	6.119	0.260	5.998	0.007	6.078	0.235	x	
	6.239	0.124	6.203	0.269	6.205	0.130	6.169	0.212	y	
	ΔE_T(eV) 1.360		ΔE_T(eV) 1.684		ΔE_T(eV) 1.590		ΔE_T(eV) 1.710			

e) Phenoxazine (V)

Calcd.	$\theta=160°$ method II		$\theta=160°$ method I		$\theta=150°$ method II		$\theta=150°$ method I			Obsd. ΔE_{max} (eV) ($\log\varepsilon_{max}$)
	ΔE_S(eV)	f	ΔE_S(eV)	f	ΔE_S(eV)	f	ΔE_S(eV)	f		
	3.129	0.025	3.288	0.052	3.161	0.025	3.411	0.057	x	
	3.555	0.238	3.785	0.370	3.574	0.224	3.858	0.336	x	3.89 (3.93)
	3.944	0.004	4.182	0.020	3.949	0.007	4.206	0.026	y	
	4.864	0.163	5.113	0.233	4.863	0.159	5.143	0.226	y	5.19 (4.66)
	4.906	1.303	5.459	1.212	4.904	1.222	5.476	1.065	x	
	5.439	0.022	5.992	0.032	5.427	0.031	5.959	0.040	y	
	5.638	0.057	6.190	0.060	5.638	0.057	6.225	0.079	x	
	5.801	0.063	6.376	0.035	5.796	0.060	6.356	0.062	y	
	6.265	0.271	6.379	0.075	6.244	0.265	6.429	0.023	x	
	6.326	0.556	6.710	0.225	6.310	0.488	6.714	0.308	y	
	ΔE_T(eV) 1.480		ΔE_T(eV) 1.985		ΔE_T(eV) 1.598		ΔE_T(eV) 2.104			

a) Lowest $^3(\pi,\pi^*)$excitation energy

b) The observed spectral data of I, II, and III are quoted from:
B. Lamatte *et al.*, *J. Chim. Phys.*, **63**, 369 (1966).
Those of IV from: R. J. Warren *et al.*, *J. Pharm. Sci.*, **55**, 144 (1966).
Those of V from: M. P. Olmsted *et al.*, *J. Org. Chem.*, **26**, 1901 (1961).
Here, the 4.13 eV band of I alone is taken from: L, Lang,
"Absorption Spectra in the Ultraviolet and Visible Region," Part II, Akadémiai Kiado, Budapest (1961).

In the extended Hückel method[13] parametrizations of the Coulomb integrals are done with the data by Pritchard and Skinner.[14]

All the bond lengths in the aromatic ring are assumed to be 1.395 Å, and the C–H and N–H bond lengths are taken to be 1.08 and 1.012 Å, respectively. The intramolecular coordinate axes and numbering of the related molecules are given in Fig. 1.

Results and Discussion

Electronic Spectra. In this calculation the dihedral angle is varied in the range 180—120°. Table 1 shows the dihedral angle dependency of the calculated results for the second π-π^* transition, since this transition can be correlated with the longest wavelength band of each spectrum. By method I the calculated value of the transition energy is in the order I<IV<II<V<III, and by method II in the order V<IV<III<II<I. We see that method I indicates more clearly the effects of the folded structure upon the calculated values of the transition energy and oscillator strength.

Table 2 shows the calculated results obtained in a proper range of the dihedral angle as compared to experimental data. It is known that method I gives superior results for molecules not containing the sulfur atom, and method II for the sulfur-containing molecules. As for thianthrene, all the observed values of the transition energies except the lowest value are in good agreement with the values calculated by method II at the dihedral angle 120—130°. The lowest observed bands of thianthrene and phenoxathiin appear to be correlated with both the second and third transi-

13) R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963); *ibid.*, **40**, 2745 (1964).
14) H. O. Pritchard and H. A. Skinner, *Chem. Rev.*, **55**, 745 (1955).

tions. In fact, the polarized excitation spectrum of phenoxathiin indicates that the lowest observed band consists of perpendicularly polarized transitions which may be assigned to the second and third transitions.[15] The observed bands of diphenylene dioxide except the band at 4.29 eV are in good accord with the transitions calculated by method I at the dihedral angle 180—170°. It should be mentioned that the third transition of diphenylene dioxide, which is forbidden at planar structure, is slightly enhanced by molecular deformation.

The lowest observed bands of phenothiazine and phenoxazine can be well correlated with the second transition. The second observed bands of these molecules are situated fairly close to both the fourth (y-polarized) and fifth (x-polarized) transitions. In fact, the polarized excitation spectra of these molecules indicate that the second observed bands are composed of two transitions with perpendicular polarization directions.[15] On the other hand, the calculated values of lowest $^3(\pi,\pi^*)$ excitation energy tend to become lower than the experimental values, *i.e.*, 2.4 eV for phenothiazine and 2.6 eV for phenoxazine.[16]

In conclusion, the present calculations on the electronic spectra show that the folded structure is prominently associated with the sulfur-containing molecules in line with the experimental results on dipole moment or crystal structure.[17] Thus, it can be said that the p-orbital model of the sulfur atom adopted is enough for explanation of the electronic spectra.

Table 3. Dihedral angle dependence of the all valence-electronic energies

	Thianthrene (I) eV	Phenoxathiin (II) eV	Diphenylene Dioxide (III) eV
180°	−1184.431	−1233.889	−1281.491
170°	−1185.215	−1234.233	−1281.468
160°	−1183.537	−1233.368	−1281.391
150°	−1181.336	−1231.310	−1281.007
140°	−1179.578	−1231.046	−1280.076
120°	−1170.391	−1227.691	−1279.784

	Phenothiazine (IV)
H intra	−1189.404 eV
H extra	−1189.193

All Valence-electronic Structures and Ionization Potentials. All the valence-electronic structures of the molecules treated herewith are considered to depend sensitively on the dihedral angle through the change in the hybridization state of the central heteroatoms. Hence, a comparative survey on the electronic structure of typical molecules is made using the extended Hückel

Table 4. Calculated and experimental results of ionization potentials

a) Calculated data by the EHT method.

Thianthrene (I)

	I_p(eV)	HOMO coefficients of the 10th heteroatom			
		S(3s)	S(3P_x)	S(3P_y)	S(3P_z)
180°	9.838	0.000	0.000	0.000	0.371
160°	9.812	0.026	0.000	−0.184	0.349
140°	9.808	0.035	0.000	−0.302	0.326

Diphenylene dioxide (III)

	I_p(eV)	HOMO coefficients of the 10th heteroatom			
		O(2S)	O(2P_x)	O(2P_y)	O(2P_z)
180°	12.225	0.000	0.000	0.000	−0.264
160°	12.265	0.010	0.000	0.042	−0.259
140°	12.380	0.018	0.000	0.087	−0.242

Phenothiazine (IV)

	I_p(eV)	HOMO coefficients of the heteroatoms							
		N(2S)	N(2P_x)	N(2P)$_y$	N(2P_z)	S(3S)	S(3P_x)	S(3P_y)	S(3P_z)
H intra	10.253	−0.053	0.000	−0.080	−0.167	0.063	0.000	0.492	−0.299
H extra	10.143	0.013	0.000	−0.249	−0.123	0.077	0.000	0.513	−0.236

b) Calculated data by the P–P–P method

Calcd. by the method I

	(I)	(II)	(III)	(IV)	(V)
180°	5.444 eV	6.494	7.962	6.093	7.342
160°	5.520	6.566	8.034	6.162	7.406
140°	5.767	6.799	8.267	6.387	7.612

Calcd. by the method II

	(I)	(II)	(III)	(IV)	(V)
180°	8.350 eV	8.395	8.435	8.077	8.090
160°	8.375	8.420	8.459	8.099	8.118
140°	8.449	8.494	8.533	8.164	8.183

c) experimental data

Thianthrene (I)	7.80 eV	
Phenoxathiin (II)	7.98	Taken from: B. Lamatte *et al.*, *J. Chim. Phys.*, **63**, 369 (1966).
Diphenylene dioxide (III)	8.10	
phenothiazine (IV)	7.28	Taken from: M.Kinoshita, This Bulletin, **35**, 1609 (1962).

15) H. H. Mantsch and J. Dehler, *Can. J. Chem.*, **47**, 3173 (1969).
16) J. M. Lhoste, M. Ptak, and D. Lexa, *J. Chim. Phys. Physicochim. Biol.*, **65**, 1876 (1968).
17) From a summary of the data in (1) and (2), it is known that diphenylene dioxide is nearly planar, and the dihedral angle for thianthrene and phenoxathiin is 120—130° and that for phenothiazine 140—150°.

theory (EHT). The valence angle of the heteroatoms in a non-folded molecule is tentatively taken to be 120°, since it is not known which value of the valence angle would be appropriate for this case.

Table 3 shows the dihedral angle dependency of the all valence electronic energy. The energy values for thianthrene and phenoxathiin are liable to yield a slight energy minimum around the dihedral angle 170°, but those for diphenylene dioxide go on increasing as the molecule folds. This theoretical finding appears to be in line with the fact that the former two molecules have appreciably folded structures. Conclusive remarks about the dihedral angle dependency of the stability of the folded structure should be avoided, because the strain energy term possibly due to the difference between the assumed and preferred values of the C–S–C bond angle is neglected.

EHT calculations on the two possible spacial configurations of phenothiazine, to be referred to as H intra and H extra according to the notation by Malrieu and Pullman,[5] indicate that the all valence electronic energy of H intra is by 0.2 eV lower than that of H extra in agreement with the ordering of the HMO energies they obtained.

Vertical ionization potentials calculated by Koopmans' theorem are given in Table 4. The values obtained by the EHT method are considerably higher than the experimental data. The dihedral angle dependency of the atomic orbital coefficients of the heteroatoms in the highest occupied molecular orbitals (HOMO) is also given for thianthrene, diphenylene dioxide and phenothiazine because these molecules are known to be typical electron-donors. The EHT ionization potential of thianthrene tends to diminish by molecular deformation. The decrease is accompanied by increase of the S($3P_y$) coefficient and decrease of the S($3P_z$) coefficient. On the other hand, the HOMO coefficient of the oxygen atom in diphenylene dioxide is largely concentrated upon the $2P_z$-orbital. This might indicate that the effect of the lone-pair orbital hybridization to electron donating property is associated with thianthrene to a greater extent than with diphenylene dioxide. The EHT ionization potential of phenothiazine is slightly lowered in going from H intra to H extra. This is followed by a remarkable increase of the N($2P_y$) orbital component in the HOMO. The ionization potentials calculated by the P–P–P method increase with the degree of folding of the molecules. The data calculated by method II well fit the relative ordering of the experimental data.

Chemical Reactivity. The P–P–P method has been found useful for explaining the observed electronic spectra. A brief comment is given on the chemical reactivities in terms of the reactivity indices obtained from the SCF MO coefficients. These heterocyclic molecules are characterized by enhanced electrophilic substitution reactions and ready formation of charge-transfer complexes. The frontier electron densities for electrophilic reaction ($f_r^{(E)}$) were calculated. The $f_r^{(E)}$ values do not change much by the change of dihedral angle (Table 5). The data on phenothiazine and phenoxazine calculated by method II well explain the fact that position 3 is a preferable site for electrophilic reagents in a number of electrophilic reactions. The calculated data on diphenylene dioxide and thianthrene indicate that the β-position is the preferable site for electrophilic attack. The calculated data on phenoxathiin can not explain the fact that electrophilic substitutions such as bromination, formylation or chloromethylation proceed at positions 2 or 8, *i.e.*, *para* to the oxygen atom. Such unexpected directing effects of the oxygen atom have been attributed by Mantsch and Dehler to the formation of a stable complex at the sulfur atom, such as evidenced by an isolable phenoxathiin-dibromide complex.[15]

TABLE 5. FRONTIER ELECTRON DENSITY VALUES FOR ELECTROPHILIC ATTACK CALCULATED WITH THE P–P–P METHOD

	position	method I		method II	
		$\theta=180°$	$\theta=120°$	$\theta=180°$	$\theta=120°$
Thianthrene (I)	1	0.077	0.042	0.017	0.013
	2	0.063	0.054	0.056	0.057
Phenoxathiin (II)	1	0.094	0.077	0.018	0.014
	2	0.020	0.014	0.061	0.061
	3	0.105	0.101	0.060	0.062
	4	0.008	0.000	0.018	0.013
Diphenylene	1	0.017	0.007	0.019	0.015
Dioxide (III)	2	0.064	0.065	0.065	0.067
Phenothiazine	1	0.027	0.010	0.037	0.033
(IV)	2	0.086	0.076	0.040	0.038
	3	0.034	0.029	0.068	0.069
	4	0.083	0.056	0.011	0.006
Phenoxazine (V)	1	0.047	0.040	0.038	0.035
	2	0.037	0.027	0.044	0.041
	3	0.079	0.080	0.071	0.072
	4	0.009	0.000	0.012	0.007

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