BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 43 3929—3932 (1970)

The Electronic Structures and Chemical Properties of O, S Containing Six-membered Heterocycles and Their Benzo-derivatives

Mamoru KAMIYA

Shizuoka College of Pharmacy, Oshika, Shizuoka-shi

(Received May 28, 1970)

It is known that compounds such as 1,4-dithiadiene, -oxathiadiene and -dioxadiene and their benzo-derivatives exhibit several characteristic chemical properties related to the electronic effects of the sulfur and oxygen atoms. That is, 1,4-dithiadiene exhibits a somewhat unusual thermal stability, as was first found by Levi,[1] who reported that the molecule underwent a Friedel-Crafts reaction; later Parham *et al.* reported that the hetero-ring in benzo-1,4-dithiadiene and/or -oxathiadiene exhibited electrophilic substitutions usually associated with an aromatic character. It is also well known that dibenzo-1,4-dithiadiene has a high thermal stability and undergoes a reaction typical of an aromatic system. Such an aromaticity of these molecules, atypical of aliphatic ethers, was correlated, by Parham *et al.*, with the ability of sulfur to expand its valence shell and with the electron-releasing property of oxygen. However, the theoretical support for the observed electronic effects of the sulfur and oxygen atoms seems insufficient, though there have been a few molecular orbital studies of the electronic structure and chemical properties of these molecules, such as simple LCAO calculations neglecting σ-π interaction and the participation of sulfur *d*-orbitals on 1,4-dithiadiene[6] and dibenzo-1,4-dithiadiene,[7] and Pariser-Parr-Pople SCF calculations of 1,4-dithiadiene,[8] benzo-1,4-dioxadiene, and dibenzo-1,4-dioxadiene.[9]

1) L. Levi, *Chem. News*, **62**, 216 (1890).
2) W. E. Parham, T. M. Roder and W. R. Hasek, *J. Amer. Chem. Soc.*, **75**, 1647 (1953).
3) W. E. Parham and J. D. Jones, *ibid.*, **76**, 1068 (1954).
4) W. E. Parham, H. Wynberg and F. L. Ramp, *ibid.*, **75**, 2065 (1953).
5) W. E. Parham and G. L. Willette, *J. Org. Chem.*, **25**, 53 (1960).
6) M. M. Kreevoy, *J. Amer. Chem. Soc.*, **80**, 5543 (1958).
7) A. K. Chandra, *Tetrahedron*, **19**, 471 (1963).
8) D. S. Sappenfield and M. Kreevoy, *Tetrahedron*, **19**, Suppl. 2, 157 (1963).
9) R. J. Wratten and M. A. Ali, *Mol. Phys.*, **13**, 233 (1967).

This paper will report semiempirical SCF-MO-CI calculations on all the related molecules and will then consider generally the relative electronic effects of the sulfur and oxygen atoms.

Calculation Method

The P-P-P method,[10] with the CI procedure including all the singly-excited configurations, is used since recent SCF calculations[8,9] on the UV spectra of the related molecules indicate that if the molecule is non-planar, a treatment assuming the separability of σ and π electrons can be allowed for in the proper choice of parameters. The values of the valence-state ionization potentials (I) and the electron affinities (A) of the π-orbitals of several atoms are taken as follows, with reference to the paper of Hinze and Jaffe[11]:

I(=C-) 11.16 eV, I(-O-) 32.90 eV,
I(-S-) 23.59 eV
A(=C-) 0.03 eV, A(-O-) 11.37 eV,
A(-S-) 10.54 eV

The sulfur *d*-orbitals are not explicitly included because it has been pointed out by Johnstone and Ward that the observed π-π^* transitions of sulfur heterocycles are generally reproduced by a small variation in the core integrals.[12] The one-center repulsion integral is obtained by the I-A approximation, while the two-center repulsion integral is evaluated by the Nishimoto-Mataga formula.[13] The core resonance integral is evaluated by adopting the variable β-core approximation,[14] because the effect of the non-planarity of the molecules upon the β_{C-O} and β_{C-S} may be properly included by adjusting the parameters. At present the following equations are tentatively used for all the molecules;

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

Here, P_{rs} corresponds to the usual π-bond order. The bond lengths of all the molecules are taken as 1.395 Å.

Results and Discussion

Electronic Spectra. The theoretical findings on the singlet π-π^* transition energy and oscillator strength are given in table 1, together with the available experimental data. The relative ordering of the intensities of the first allowed transitions of 1,4-dioxadiene and -dithiadiene is predicted correctly, and it is found that the introduction of the oxygen atom causes increase in the first allowed transition energy. As regards benzo-1,4-dithiadiene the assignment of the three observed bands is straight foward because of the agreement between the predicted and observed orderings of the absorption intensity. The effect of the hetero-ring structure upon the oscillator strength of the first allowed transition is quite decreased from the monocyclic molecule to the monobenzo-derivatives. In the case of benzo-1,4-oxathiadiene, the polarization direction of the second allowed transition (5.08 eV) is varied to such an extent that the transition moment makes an angle of 68° to the *x*-axis. This is interesting because it suggests that a shortly polarized structure, such as  , contributes to the excited state, just as is to be expected from the relative electron-releasing order of the sulfur and oxygen atoms.

In the case of the dibenzo-derivatives also, the calculated spectra well reflect the effect of hetero-atom replacement. In dibenzo-1,4-oxathiadiene, the first two forbidden bands are little enhanced through the lowering of the molecular symmetry. In dibenzo-1,4-dioxadiene, the observed band at 4.29 eV was assigned by Wratten and Ali[9] to the second forbidden band, which becomes allowed through a slight folding about the line joining the heteroatoms. It is of interest to note that the second and third allowed transitions, with very different intensities, tend to degenerate in all the calculated spectra and to change their mutual order from dibenzo-1,4-dioxadiene to the other two molecules.

Ionization Potentials. The negatives of the ho and lv orbital energies are given in table 2, together with the available experimental data on ionization potentials. It is usually accepted that the ionization potentials calculated by Koopman's Theorem are 1—2 eV too large in comparison with the experimental values; such is also true for the present results. Interestingly, the effect of the hetero-ring structure upon the calculated ionization potentials and electron affinities is almost independent of the introduction of a benzene-ring. The calculated ionization potentials of the dibenzo-derivatives exhibit an ordering identical to that of the experimental values determined by the electron-impact method.

Electron Distributions. The calculated findings on the π-electron densities and π-bond orders are shown in Fig. 1. First, it is established that the sulfur atom in monocyclic molecules more

10) R. Pariser and R. G. Parr, *J. Chem. Phys.*, **21**, 466,767 (1953); J. A. Pople, *Trans. Faraday Soc.*, **49**, 1375 (1953).
11) J. Hinze and H. H. Jaffe, *J. Amer. Chem. Soc.*, **84**, 540 (1962).
12) R. A. W. Johnstone and S. D. Ward, *Tetrahedron*, **25**, 5484 (1969).
13) K. Nishimoto and N. Mataga, *Z. Physik. Chem.*, **12**, 335 (1957).
14) K. Nishinoto and L. S. Forster, *Theoret. Chim. Acta*, **4**, 155 (1966).

TABLE 1. CALCULATED AND EXPERIMENTAL DATA OF ELECTRONIC SPECTRA

	Calculated			Experimental	
	ΔE_s	Sym.	f	ΔE_s	$\log \varepsilon_{max}$
1,4-Dioxadiene [1]	2.72	(B_{1g})	—		
	5.13	(B_{2u})	0.13	~4.96	~3.0[a]
	7.54	(B_{2u})	1.38		
1,4-Oxathiadiene [2]	2.92	(B_2)	0.00		
	5.00	(A_1)	0.15		
	7.41	(A_1)	1.22		
1,4-Dithiadiene [3]	3.07	(B_{1g})	—		
	4.87	(B_{2u})	0.18	4.59[b]	3.65[c]
	7.12	(B_{3u})	0.24	5.748	—
Benzo-1,4-dioxadiene [4]	3.15	(B_2)	0.00		
	3.75	(A_1)	0.08		
	5.19	(B_2)	0.14		
	5.27	(A_1)	0.53		
	5.83	(B_2)	0.04		
Benzo-1,4-oxathiadiene [5]	3.27	(A)	0.00		
	3.77	(A)	0.08		
	5.08	(A)	0.18		
	5.21	(A)	0.44		
	5.81	(A)	0.05		
Benzo-1,4-dithiadiene [6]	3.37	(B_2)	0.00		
	3.78	(A_1)	0.08	4.12	2.91[d]
	4.97	(B_2)	0.18	4.73	3.81
	5.14	(A_1)	0.40	4.90	4.23
	5.80	(B_2)	0.05		
Dibenzo-1,4-dioxadiene [7]	3.51	(B_{1g})	—		
	3.75	(B_{3u})	0.19	4.13	[e]
	4.08	(A_g)	—	4.29	3.87
	5.07	(B_{3u})	1.50	5.44	4.73
	5.11	(B_{2u})	0.14	5.58	4.64
	5.63	(B_{1g})	—		
	5.75	(A_g)	—		
	5.85	(B_{2u})	0.78	6.11	
Dibenzo-1,4-oxathiadiene [8]	3.59	(B_2)	0.00		
	3.79	(B_2)	0.17	4.20	3.60[e]
	4.06	(A_1)	0.00		
	5.00	(A_1)	0.14	5.14	4.50
	5.04	(B_2)	1.37	5.21	4.50
	5.54	(A_1)	0.03	5.64	
	5.73	(B_2)	0.02		
Dibenzo-1,4-dithiadiene [9]	3.66	(B_{1g})	—		
	3.81	(B_{3u})	0.16	~4.13	~2.9[f]
	4.05	(A_g)	—		
	4.90	(B_{2u})	0.16	4.81	4.60[e]
	5.01	(B_{3u})	1.27	5.10	
	5.45	(B_{1g})	—		
	5.70	(A_g)	—		
	5.81	(B_{2u})	0.12	5.93	

ΔE_s = transition energy (eV).

f = oscillator strength, where the basic transition moment of $i \rightarrow j$ singly excited transition is calculated by the equations: $m_x = \sum_r \sqrt{2} c_r^i c_r^j \bar{x}_{rr}$, $m_y = \sum_r \sqrt{2} c_r^i c_r^j \bar{y}_{rr}$, $m_z = 0$.

sym. = transition symmetry denoted from planar structure.

a) L. W. Pickett and E. Sheffield, *J. Org. Chem.*, **68**, 216 (1946).

b) Reference 8. c) Reference 4. d) Reference 2.

e) B. Lamatte and G. Berthier, *J. Chim. Phys.*, **63**, 369 (1966).

f) L. Lang, "Absorption Spectra in the Ultraviolet and Visible Region," Part II, Akadémiai Kiadó, Budapest (1961).

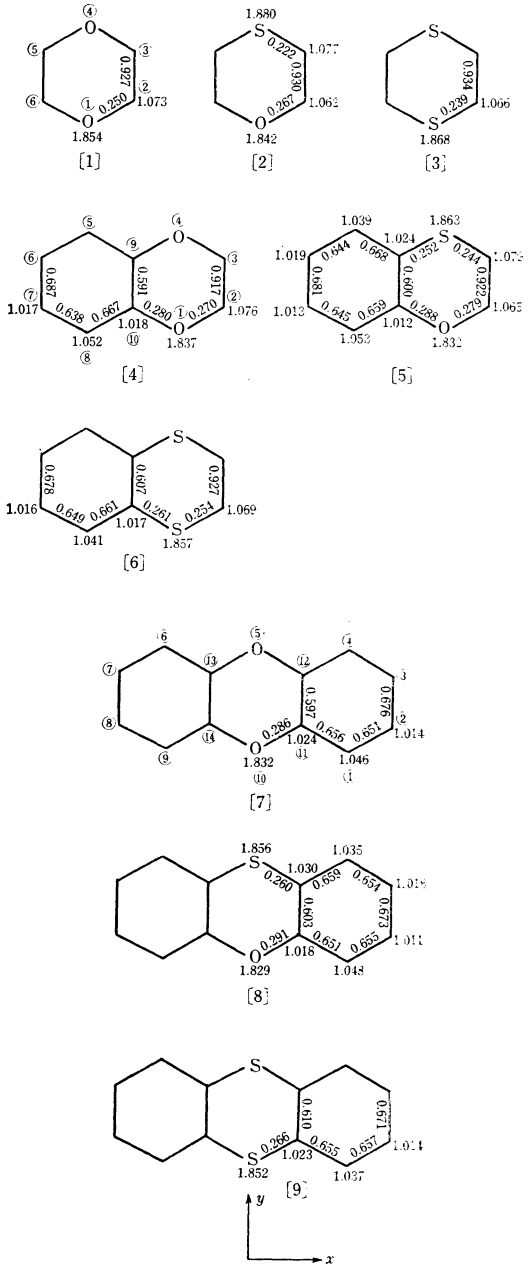

Fig. 1. π-Electron density and π-bond order.

Table 2. Theoretical and experimental data on ionization potential (I_p) and electron affinity (E_A)

Compound	Calcd. I_p (eV)	Calcd. E_A (eV)	Obsd. I_p (eV)
[1]	7.71	0.75	
[2]	7.74	0.68	
[3]	7.74	0.58	
[4]	8.11	1.13	
[5]	8.09	1.06	
[6]	8.07	0.98	
[7]	8.43	1.33	8.10*
[8]	8.39	1.26	7.98
[9]	8.35	1.17	7.80

* Evaluated from electron-impact method. B. Lamatte and G. Berthier, *J. Chim. Phys.*, **63**, 369 (1966).

favours the fixation of the diene-structure. It is of interest to note that such a difference between the sulfur and oxygen atoms is more enlarged in the hetero-ring containing both hetero-atoms. The same thing is true for the benzo-derivatives. In the case of benzo-1,4-dithiadiene, the predicted site for electrophilic attack, C-2(3) in the hetero-ring, is in agreement with that observed by Parham *et al.*[2-5] A further prediction from the electron distributions is that the electrophilic substitutions of benzo-1,4-oxathiadiene and/or -dioxadiene should also occur at the hetero-ring. As regards the dibenzo-derivatives, it is found that a characteristic relation, $P^{\pi}{}_{\beta-\beta} > P^{\pi}{}_{\alpha-\beta}$, previously noted as a result of a simple LCAO calculation of Chandra[7] is also valid for all the molecules, and that this tendency is slightly promoted by the presence of an oxygen atom.

The present calculations were carried out with an HITAC 5020-E computer at the Computation Center of the University of Tokyo. The author wishes to thank Professor Y. Akahori for his interest and valuable discussions.