tetrachlorobiphenylene-2,2′ sulfite, 33483-00-0; *o*-phenylene sulfate, 4074-55-9; biphenylylene-2,2′ sulfate, 31268-08-3; 4-nitro-*o*-phenylene sulfite, 33483-03-3; 4,4′-dimethoxybenzophenone-2,2′ sulfite, 33483-04-4; 3,4-dichlorocyclopentadienone dimer, 33483-05-5; 1-hydroxydibenzofuran, 33483-06-6.

A Semiempirical Molecular Orbital Study of *o*-Phenylene Carbonate and *o*-Phenylene Sulfite[1]

D. C. DEJONGH*[2] AND M. L. THOMSON

Department of Chemistry, Wayne State University, Detroit, Michigan 48202

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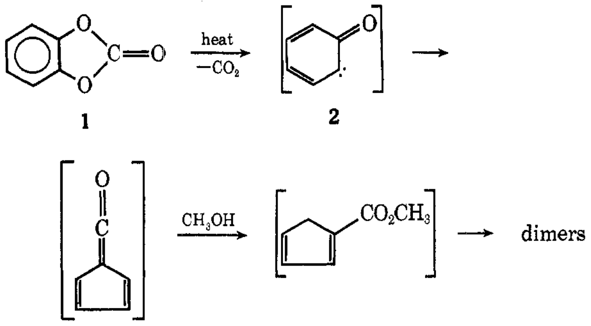
A molecular orbital approach to the rationalization of the preferential loss of CO_2 upon pyrolysis of *o*-phenylene carbonate and from its molecular ions and of the preferential loss of SO from the corresponding species of *o*-phenylene sulfite is reported. Overlap populations obtained from a CNDO/2 program are used as indications of total bond strengths. Also, minimum energies of the species produced by competing fragmentation pathways are compared.

The mass spectrum and gas-phase pyrolysis of *o*-phenylene carbonate (**1**)[3] have been reported. The molecular ion of **1** forms an ion C_6H_4O of major intensity upon loss of CO_2, at *m/e* 92, along with a metastable ion; it also loses CO to a minor extent, forming an ion $C_6H_4O_2$ at *m/e* 108. If **1** is pyrolyzed in a stream of nitrogen with CH_3OH in the stream, the major products are the dimers of methyl cyclopentadiene-1-carboxylate (44%) (eq 1). Thus, CO_2, rather than CO, is preferentially lost from **1** pyrolytically as well as from the molecular ions.

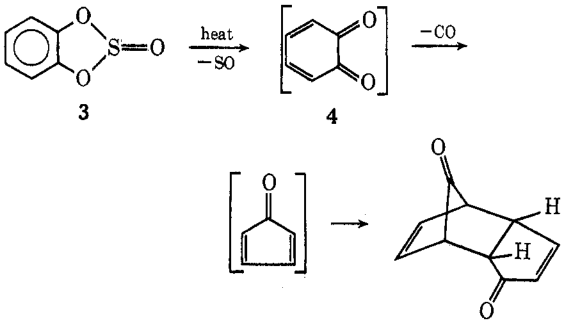


1 **2**

(1)

On the other hand, *o*-phenylene sulfite (**3**)[4,5] and substituted analogs[6] preferentially lose SO rather than SO_2. The major loss from the molecular ion of **3** is SO to form a $C_6H_4O_2$ ion at *m/e* 108 along with the corresponding metastable ion. A minor loss of SO_2 occurs without a metastable ion to form an ion C_6H_4O at *m/e* 92. When **3** is pyrolyzed in a stream of nitrogen, SO, followed by CO, is lost and cyclopentadienone forms, which dimerizes (80%) (eq 2).

In summary, the major path from **1** corresponds to the minor path from **3**, and vice versa. In this article we report a molecular orbital approach toward the rationalization of the preferential loss of CO_2 from **1** and the preferential loss of SO from **3**.



3 **4**

(2)

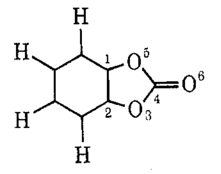
Experimental Section

Mass spectra, pyrolysis results, and syntheses of **1** and **3** have been reported elsewhere.[3-5] Calculations were obtained on an IBM 360/67 computer at the Wayne State University Computing and Data Processing Center.

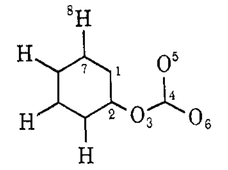
Pople and Beveridge's CNDO/2 program[7] was used to calculate Mulliken overlap populations and total energies.[8] The overlap populations were used as an indication of total bond strengths.[9] There has been a substantial amount of controversy as to whether 3d orbitals should be included to represent third-

TABLE I

OVERLAP POPULATIONS FROM CALCULATIONS MADE ON 1



1



1a

Structure	Charge	Overlap population for bond 1–5, 2–3	3–4, 4–5	2–3	3–4
1	0	0.817	0.914		
1	+1	0.822	0.941		
1a[a]	0			0.932	0.891
1a[a]	+1			0.922	0.911
1a[b]	0			1.026	0.893
1a[b]	+1			0.994	0.898

[a] A planar benzenoid-type geometry was used for the ring. [b] A carbenoid-type geometry was used for the ring.

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(1) This work was supported in part by the National Institutes of Health.

(2) To whom correspondence should be addressed: Département de Chimie, Université de Montréal.

(3) (a) D. C. DeJongh and D. A. Brent, *J. Org. Chem.*, **35**, 4204 (1970). (b) D. C. DeJongh, D. A. Brent, and R. Y. Van Fossen, *ibid.*, **36**, 1469 (1971).

(4) D. C. DeJongh, R. Y. Van Fossen, and C. F. Bourgeois, *Tetrahedron Lett.*, 271 (1967).

(5) D. C. DeJongh, R. Y. Van Fossen, and A. Dekovich, *ibid.*, 5045 (1970).

(6) D. C. DeJongh and R. Y. Van Fossen, *J. Org. Chem.*, **37**, 1129 (1972).

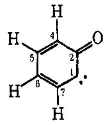
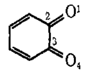
(7) J. A. Pople and D. L. Beveridge, "CINDO," Quantum Chemistry Program Exchange, Department of Chemistry, Indiana University, No. 141.

(8) R. S. Mulliken, *J. Chem. Phys.*, **23**, 1841 (1955).

(9) Previously, π-bond orders have been used as indication of bond strengths; see R. C. Dougherty, R. L. Foltz, and L. B. Kier, *Tetrahedron*, **26**, 1989 (1970).

TABLE II

MINIMUM ENERGIES

	Energy, kcal	Charge		Energy, kcal	Charge
CO_2	−27,367.8	0	CO	−15,719.2	0
SO_2	−29,849.7[a]	0	SO	−18,270.7[a]	0
 2	−39,876.9 −39,675.8	0 +1	 4	−51,503.8 −51,258.8	0 +1

[a] From the unmodified program.

TABLE III

FINAL GEOMETRIES WHICH GIVE MINIMUM ENERGIES

A. Bond Lengths

	Bond length, Å					
Compd[a]	1–2	2–3	3–4	4–5	4–6	1–5
1		1.360	1.312	1.312	1.233	1.360
1a (carbenoid)		1.290	1.320	1.260	1.260	
1a (benzenoid)		1.290	1.316	1.260	1.260	
2[b]		1.150				
3[c]		1.400	1.590	1.590	1.390	1.400
3a[c]		1.400	1.590		1.390	1.400
4	1.150		1.150			
CO	1.128[d]					
CO_2	1.160[d]					
SO	1.400[e]					
SO_2	1.432[e]					

B. Bond Angles

	Bond angle, deg					
Compd	512	123	234	345	451	546
1	108	108	105	114	105	123
1a (carbenoid)[b]		120	109.5	120		120
1a (benzenoid)		120	109.5	120		120
2[b]		120				
3[c]	111	112	108.6	97.1	108.6	109.8
3a[c]	128	117			108.6	109.8
4		120				
CO_2	180					
SO_2	120[e]					

C. Dihedral Angles

	Dihedral angle, deg[f]				
Compd	7–3	1–4	2–5	2–6	8–2
1a[b]	220	0	0	180	150
2	220				
3[c]	180	352	1	259	
3a[c]	180	352	1	259	

[a] The benzene ring used was a regular planar hexagon with C–C = 1.394 Å and C–H = 1.084 Å unless noted otherwise. [b] A carbenoid benzene ring was considered. The C=C = 1.336 Å; C–C = 1.54 Å. All angles were 120° except the angle at the carbene center (109.5°). The ring is not planar but has dihedral angles approximately 10–30° above or below the mean plane of the ring. [c] The modified program was used on these structures. [d] Reference 14. [e] L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1960, p 329. [f] Structures not presented in this section were taken as planar compounds.

row elements.[10,11] We have also used a modified program in which the effect of 3d orbitals was removed by altering the number of $n = 3$ level orbitals from nine to four in the subroutine INTGRL. The removal of these d orbitals has no effect on calculations that concern the first row elements only.

The molecular coordinates were calculated internally from bond angles and bond lengths.[12] The structure of *o*-phenylene sulfate, as determined by X-ray analysis,[13] was used as a starting point for *o*-phenylene sulfite (**3**). Standard bond lengths and angles were used as the starting point for *o*-phenylene carbonate (**1**).[14] The geometries were then systematically varied to achieve a minimum total energy for the system. Overlap populations for bonds at the geometries giving minimum energies are reported in Tables I and IV. Overlap populations for the neutral molecules and for the species with charges of +1 were calculated. Table II contains the minimum energies calculated for the products of the competing pathways, and Table III contains the geometries used to calculate these energies and the overlap populations.

Results and Discussion

_o_-Phenylene carbonate (1).—In Table I are listed the overlap populations for bonds of the heterocyclic portion of **1** and its +1 charged species. The bond with the lowest overlap population is 1–5; it is therefore the weakest bond in the heterocyclic ring. Table I also contains calculations made on the intermediate **1a** which would be formed by cleavage of bond 1–5. The bond with the lowest overlap population in **1a** is 3–4 when either carbenoid or benzenoid geometry is used for the ring. Thus, the molecular orbital study indicates that the neutral and +1 charged species corresponding to **1** would preferentially eliminate CO_2. This is also the experimental observation, as described in eq 1.

In Table II are the minimum energies calculated for the species which would be produced upon competitive elimination of CO and CO_2 from **1**. The sum of the energies of CO_2 and **2** (uncharged) is 21.7 kcal lower than the sum of the energies of CO and **4** (uncharged). The corresponding value is 65.6 kcal when the energies of the +1 charged species of **2** and **4** are used. Therefore, this comparison also predicts that the loss of CO_2 would be the preferred path in pyrolysis and in the mass spectrometer.

The final geometries of **1**, **1a**, **2**, and **4** which give the lowest energies are given in Table III. The bond lengths and angles can be varied by approximately 5% without changing the relative ordering of the overlap populations.

_o_-Phenylene Sulfite (3).—The sum of the energies in Table II for SO and **4** (uncharged) is 47.9 kcal lower than the sum of the energies of SO_2 and **2** (uncharged). Thus, the comparison of minimum energies predicts that SO would be lost in preference to SO_2, and this is the behavior observed upon pyrolysis. When the

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[10] D. P. Santry and G. A. Segal, *J. Chem. Phys.*, **47**, 158 (1967).

[11] A. Rauk, S. Wolfe, and I. G. Csizmadia, *Can. J. Chem.*, **47**, 113 (1969), and references cited therein.

[12] M. J. S. Dewar and N. C. Baird, "Atomic Cartesian Coordinates for Molecules," Program 136, Quantum Chemistry Program Exchange, Department of Chemistry, Indiana University.

[13] F. P. Boer and J. J. Flynn, *J. Amer. Chem. Soc.*, **91**, 6604 (1969).

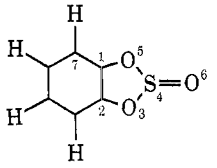
[14] "Table of Interatomic Distances and Configurations in Molecules and Ions," L. E. Sulton, Ed., Special Publications No. 11 and 18, The Chemical Society, London, 1958 and 1965.

energies of the +1 charged species of **4** and **2** are used, the sum of the energies of SO and **4** (charged) is 4 kcal lower than the sum of the energies of SO_2 and **2** (charged). The preferred loss upon electron impact is SO. Geometries of **2** and **4** are given in Table III.

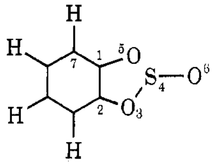
In Table IV are listed the overlap populations obtained from **3** and **3a** using the geometries given in Table III. The program which was modified to exclude contributions from d orbitals was used. The weakest bond in **3** is the S–O bond of the ring, rather than the C–O bond. For intermediate **3a**, which would form from cleavage of this S–O bond, the calculations show that cleavage of the bond with the lowest overlap population would lead to expulsion of SO from both the charged and the uncharged species. This is the behavior observed experimentally, as described in eq 2. If contributions from d orbitals are included, the overlap populations of the bonds between S and O increase, since the net overlap of all the orbitals on S and O is greater if d orbitals are included.

Table IV

Overlap Populations from Calculations Made on **3**



3



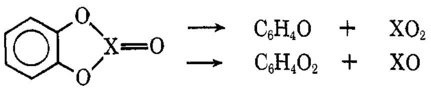
3a

Structure	Charge	Overlap population for bond[a] 1–5, 2–3	3–4, 4–5	2–3	3–4
3	0	0.822	0.620		
3	+1	0.799	0.638		
3a	0			0.813	0.646
3a	+1			0.804	0.642

[a] The program modified to exclude d orbitals was used.

Thus, relating overlap populations to relative bond strengths for bonds involving two different sets of atoms, *i.e.*, C–O and S–O in **3**, might not be so meaningful as in the case of **1** where only C–O bonds are compared. However, the comparison of the sums of the energies of the species produced by the competing losses of SO and SO_2 gives the same qualitative results.

In summary, there are two competing pathways experimentally observed for fragmentation of system **5** upon pyrolysis and electron impact. When X = C, the loss of XO_2 is preferred and when X = S, the loss of XO is preferred. The molecular orbital approach described here rationalizes this behavior both in terms of relative bond strengths and energies of the species produced by the competing paths.



5

Registry No.—**1,** 2171-74-6; **3,** 6255-58-9.

Acknowledgment.—We wish to thank Drs. P. A. Scheer and A. Tannin for helpful discussions. We also wish to acknowledge the service of the Wayne State University Computing and Data Processing Center.

A Free Electron Molecular Orbital Model of Aromaticity

William D. Hobey

Department of Chemistry, Worcester Polytechnic Institute, Worcester, Massachusetts 01609

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Breslow's criterion for aromaticity applied to the simplest FEMO model yields results for single ring molecules in conformity with the literature. In particular, it is shown that incompletely filled shells may produce antiaromaticity in small ring molecules, but underlying closed shells dominate in larger rings so that all annulene and polymethine series eventually become aromatic.

Although the free electron molecular orbital (FEMO) model has shown a degree of success in the interpretation of electronic spectra of conjugated systems,[1] the extension of the approach to chemical properties has given rather limited agreement. In particular, an attempt to use FEMO (in its more refined network model) to calculate resonance energies gave "surprisingly poor" results.[2] However, it is the purpose of this paper to show that FEMO can be used to analyze aromaticity, provided Breslow's recent reformulation of the criterion for aromaticity[3] is employed; *i.e.*, the π energy of a cyclic compound is compared to that of the corresponding iso-π-electronic linear compound, a decrease in π energy upon cyclization indicating aromaticity, an increase indicating antiaromaticity.

The Model.—We shall use in this paper FEMO in its simplest form. The behavior of the π electronic wave functions perpendicular to the carbon skeleton is assumed to be separable from the behavior along the bonds, and to be constant for all π systems considered. Consequently, this component is ignored in all subsequent considerations. For the component along the carbon skeleton the actual periodic potential energy function is replaced by a constant, taken to be zero for convenience; *i.e.*, straight-chain systems are treated as electrons in a linear box while cyclic systems are treated as electrons on circular rings.

The one remaining assumption for each type of molecule is the effective length of the π system. To avoid prejudicing our results, we adopt two assumptions found in the literature. Throughout this paper we will assume all C–C bonds, whether in a straight

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[1] A review of the method is given by N. S. Bayliss, *Quart. Rev., Chem. Soc.*, **6**, 319 (1952). A collection of papers has been reprinted: J. R. Platt, *et al.*, "Free-Electron Theory of Conjugated Molecules," Wiley, New York, N. Y., 1964.

[2] C. W. Scherr, *J. Chem. Phys.*, **21**, 1413 (1953).

[3] R. Breslow, *Chem. Eng. News*, **43** (26), 90 (1965); *Chem. Brit.*, **4**, 100 (1968); *Angew. Chem., Int. Ed. Engl.*, **7**, 565 (1968).