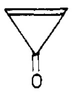
Thiirene Dioxides. Electronic Structure[1]

Claus Müller,[2] Armin Schweig,* and Hans Vermeer

Contribution from the Fachbereich Physikalische Chemie, Universität Marburg, D-3550 Marburg/Lahn, Germany. *Received July 26, 1974*

Abstract: The thiirene dioxide system is investigated both theoretically and by uv photoelectron spectroscopy. Both approaches reveal a strong hyperconjugative interaction between the occupied C=C π MO and an occupied SO_2 σ MO. Moreover, there is a modest mixing between the C=C π MO and a vacant SO_2 σ^* MO which is a nearly pure sulfur d AO. This latter $\pi\sigma^*$ interaction is responsible for a tiny π charge transfer from the C=C double bond to the SO_2 unit. Its extent is compared with the corresponding π electron transfer in other unsaturated cyclic sulfones and annulenones. The results suggest that the tendency of these systems to exhibit properties expected of an "aromatic" model is: cyclopropenones > tropone > thiirene dioxides. The study further shows that the major interactions between the ethylene and sulfonyl moieties in the thiirene dioxides on the one hand and the ethylene and carbonyl groups in the cyclopropenones on the other are formally quite analogous and differ only in degree.

Molecules such as cyclopropenone (**1**) and thiirene dioxide (**2**) are formally composed of an ethylene unit and a carbonyl or sulfonyl unit, respectively. The interactions between these units may be inductive and/or conjugative. Taking the ethylenic π ($\pi_{C=C}$) MO as a probe for these interactions in **1** it was recently[3] suggested that the main interactive effect is the inductive influence of the carbonyl group which stabilizes the $\pi_{C=C}$ MO by about 1 eV. Further the sum of the destabilizing ($\pi_{C=C}/\pi_{C=O}$) and stabilizing ($\pi_{C=C}/\pi^*_{C=O}$) conjugative effects appeared to be only about 0.4 eV. Evidence for $\pi_{C=C}/\pi^*_{C=O}$ mixing was given suggesting that cyclopropenone, indeed, bears some resemblance to the cyclopropenyl cation (**3**).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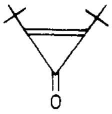
Both in the original publication[4] on thiirene dioxides and in a recent paper[5] the structural resemblance of cyclopropenones and thiirene dioxides was discussed. From a comparative study of the chemical and physical properties of both classes of compounds it was not possible to come to any firm conclusions regarding the electronic nature of the thiirene dioxides. Recently Janssen and coworkers[5] concluded that a comparison of cyclic unsaturated sulfones and ketones is of little value. Pursuing interests in quantum chemical and photoelectron (pe) spectroscopic studies of such compounds, namely cyclopropenones (**1** and **4**),[3] cyclopentadienones (**7**–**9**),[6] tropone (**12**),[7] thiophene dioxides (**10** and **11**),[8] and thiepine 1,1-dioxide (**13**),[9] we now present calculations and the results of a pe study on the remaining members of the series, the thiirene dioxides **2**, **5**, and **6** in conjunction with an investigation of the cyclopropenes **14** and **15** and the thiirane dioxide **16** as model compounds.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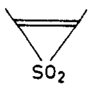
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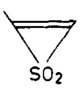
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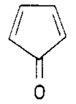
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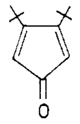
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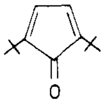
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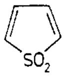
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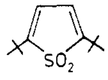
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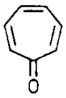
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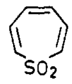
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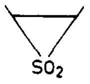
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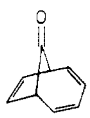
The present investigation is concerned mainly with an analysis of the inductive and conjugative interactions between the C=C and SO_2 units in the thiirene dioxides and consideration of the possible "aromaticity" of these species as well as related unsaturated sulfones and annulenones. The present treatment clearly reveals analogies and differences between the electronic structures of the cyclopropenones and the thiirene dioxides.

Calculations and Discussion

In a recent paper,[7] a method was described which permits one to interrupt the conjugation of selected parts of a molecule from the rest of the system. Using this method it is possible to distinguish inductive from conjugative effects and to evaluate such interactions. The method was successfully applied to tropone (**12**),[7] bicyclo[4.2.1]nona-2,4,7-trien-9-one (**17**),[10] 3,3,6,6-tetramethyl-1-thiacycloheptyne (**18**),[11] and cyclopropenones (**1** and **4**).[3] Figures 1 and 2 show the results of such calculations for cyclopropene (**14**) and thiirene 1,1-dioxide (**2**). The set of structural data used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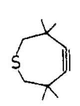
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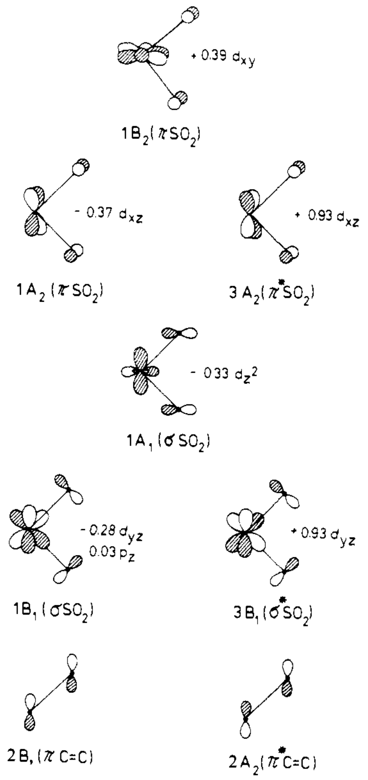
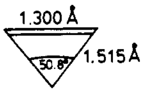


Figure 1. Highest occupied and lowest unoccupied (*) MO's of thiirene dioxide obtained for the π decoupled ethylene and SO_2 systems. The MO's are classified in terms of the symmetry species of the point group C_{2v}, of their respective π and σ nature, and of the molecular units (C=C or SO_2) where they are mostly localized. Symmetry allows only the $1A_1(\sigma_{SO_2})$ and $1B_2(\pi_{SO_2})$ MO's to extend over the whole molecule. The contributions (AO coefficients) of the respective d AO's are explicity given.

and the coordinate system chosen for **2** are illustrated in **19**,[12] **20**,[12a] and **21**, respectively. The calculations are per-



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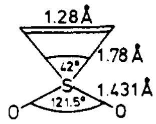

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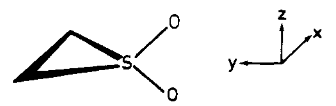

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formed by use of an extended CNDO/S method.[13] The calculations carried out for **2** with conjugatively decoupled SO_2 and ethylene units yield the highest occupied and lowest vacant (*) MO's for the SO_2 and C=C parts shown and classified[14] in Figure 1. There are six SO_2 MO's, four unoccupied and two occupied ones. The first three MO's (at the top of Figure 1), namely the $1B_2(\pi_{SO_2})$, $1A_2(\pi_{SO_2})$, and $3A_2(\pi^*_{SO_2})$ MO's, correspond to π MO's of the SO_2 molecule and the remaining ones, $1A_1(\sigma_{SO_2})$, $1B_1(\sigma_{SO_2})$, and $3B_1(\sigma^*_{SO_2})$ correspond to σ MO's. For each MO the coefficient of the contributing d AO is given. The figure indicates that the vacant MO's, $3A_2(\pi^*_{SO_2})$ and $3B_1(\sigma^*_{SO_2})$, are nearly pure d AO's and that they are simply obtained from the corresponding occupied MO's, $1A_2(\pi_{SO_2})$ and $1B_1(\sigma_{SO_2})$, by inverting the sign of the d AO coefficients.

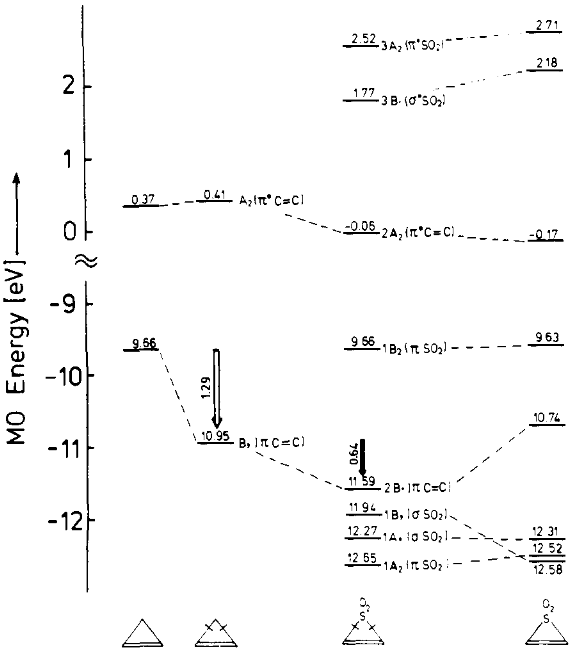

Figure 2. Interaction diagram of the respective MO's of the ethylene and CH_2 or SO_2 units. The MO's prior to interaction or those obtained when the π conjugation between both units is interrupted. The interruption is symbolized by dashes across the C-C or C-S bonds. The white and black arrows represent the calculated conjugative and inductive effects, respectively.

Thus the d AO's reinforce bonding between the sulfur and the oxygen atoms in the occupied MO's and weaken bonding in the vacant ones. For the ethylene part, only the bonding π, $2B_1(\pi_{C=C})$, and antibonding π, $2A_2(\pi_{C=C})$, MO's (illustrated at the bottom of Figure 1) are relevant.

By allowing conjugation to take place between the ethylene and SO_2 units in thiirene dioxide, which simply means that now a usual CNDO/S calculation is carried out for **2**, the MO's (illustrated in Figure 1) with the same symmetry may interact. Thus conjugative interaction between the $1B_1(\sigma_{SO_2})$, $2B_1(\pi_{C=C})$, and the $3B_1(\sigma^*_{SO_2})$ on the one hand and between the $1A_2(\pi_{SO_2})$, $2A_2(\pi^*_{C=C})$, and $3A_2(\pi^*_{SO_2})$ on the other may be anticipated. The extent of these interactions is revealed in the interaction diagram of Figure 2. It is noted that *only one interaction, namely that between the* $1B_1(\sigma_{SO_2})$ *and* $2B_1(\pi_{C=C})$ *MO's, turns out to be significant in* **2**. Besides this predominating $\sigma\pi$ (hyperconjugative) effect, an additional weak interaction with the vacant $3B_1(\sigma^*_{SO_2})$ MO is predicted. This latter interaction makes possible a transfer of π charge from the C=C to the SO_2 unit (for a more detailed discussion of this point see the last section of this report). Finally the interaction diagram indicates that the spiroconjugated[15,16] interactions between the A_2 MO's appear to be negligible.

Comparison of the interaction diagram of Figure 2 with the corresponding diagram[3] for cyclopropenone (**1**) reveals a remarkable quantitative difference: the $\sigma\pi$ interactions of the B_1 MO's in **2** which are formally analogous to the $\pi_{C=O}/\pi_{C=C}/\pi^*_{C=O}$ interactions in **1** are appreciably weaker than the corresponding $\pi\pi$ interactions in **1**. As a main consequence it is to be expected that the π charge transfer from the $\pi_{C=C}$ MO to the SO_2 unit will be less pronounced in **2** than the corresponding transfer to the C=O unit in **1**. This point will also be discussed more fully in the last section of this report.

Interestingly, Figure 2 further shows that the $B_1(\pi_{C=C})$ MO of cyclopropene (**14**) is strongly stabilized by interrupting the $CH_2/\pi_{C=C}$ conjugation in this molecule whereas

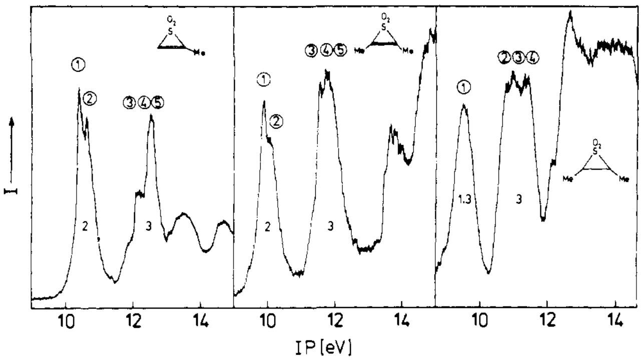

Figure 3. Photoelectron spectra of 2-methylthiirene 1,1-dioxide, 2,3-dimethylthiirene 1,1-dioxide, and *cis*-2,3-dimethylthiirane 1,1-dioxide. For the measured vertical ionization potentials and the assignment of bands, see Figures 4 and 5.

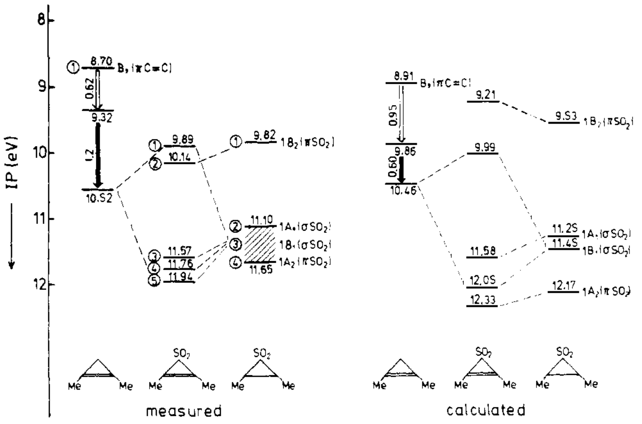

Figure 4. Measured and calculated correlation diagrams for the highest occupied MO's of *cis*-2,3-dimethylthiirane 1,1-dioxide, 2,3-dimethylthiirene 1,1-dioxide, and the π_{MO} of hypothetical 1,2-dimethylcyclopropene which is not influenced by the hyperconjugation with the methylene group but influenced by the inductive effect of the SO_2 group. These respective conjugative and inductive effects are represented by white and black arrows. The numbers shown above the levels are vertical ionization potentials.

the vacant $A_2(\pi^*_{C=C})$ MO energy remains, as expected, nearly unchanged. The calculated hyperconjugative stabilization (⇒, 1.29 eV) is in reasonable agreement with that obtained by the MINDO/2[17] (1.13 eV) method. At first glance these calculated values seem not to be in accord with the experimental[18] MO difference (0.64 eV) of cyclopropene (**14**) and ethylene (the measured ionization potentials for these molecules are shown in **22** and **23** below). The disagreement, however, completely disappears when the calculated π MO energy change (CNDO/S = 0.34 eV, MINDO/2 = 0.19 eV) caused by shortening the C–C bond length of ethylene from 1.337 to 1.300 Å (=length of the C=C double bond in cyclopropene, *cf.* **19**) is taken into account. Thus, it may reasonably be assumed that the hyperconjugative effect of the CH_2 group in cyclopropene amounts to about 1 eV. On the other hand it seems to be quite certain that the CNDO/S method tends to underestimate the inductive effect (→, 0.64 eV) of the SO_2 part (for a more detailed discussion, see the next section).


9.87 eV[19]

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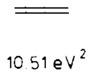
10.51 eV[20]

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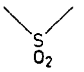
In conclusion, theory makes the following predictions regarding the electronic nature of the thiirene dioxides: (i) a strong hyperconjugative interaction between the occupied $\pi_{C=C}$ and $B_1(\sigma_{SO_2})$ MO's and (ii) a weak mixing of occupied and vacant MO's (mainly sulfur d AO's). Moreover, compared with the situation in cyclopropenone (**1**) the latter mixing is less marked in **2** implying that **2** bears less resemblance to an "aromatic" cyclic 2π system than does **1**. The method of choice for examining prediction i is photoelectron spectroscopy.

Photoelectron Spectra of 2-Methylthiirene 1,1-Dioxide (6), 2,3-Dimethylthiirene 1,1-Dioxide (5), and *cis*-2,3-Dimethylthiirane 1,1-Dioxide (16) and Discussion. Figure 3 shows the pe spectra[21] of 2-methylthiirene 1,1-dioxide (**6**), 2,3-dimethylthiirene 1,1-dioxide (**5**), and *cis*-2,3-dimethylthiirane 1,1-dioxide (**16**). The spectra of the thiirene dioxides **6** and **5** exhibit two signals with relative intensities of about 2:3 and the spectrum of the thiirane dioxide **16** similarly shows two signals with an intensity ratio of 1.3:3. From the measured relative intensity and the structure of the signals it follows that the first and second signals of **5** and **6** consist of two (1 and 2) and three bands (3 to 5), respectively. On the other hand the first and second signals of **16** consist of one (1) and three bands (2 to 4), respectively. From experience with the interpretation of the pe spectra of other sulfones, namely dimethyl sulfone (**24**),[22] methyl vinyl sulfone (**25**),[22] divinyl sulfone (**26**),[22] 2,5-di-*tert*-butylthiophene 1,1-dioxide (**11**),[8] and tetrahydrothiophene 1,1-dioxide (**27**)[8] and comparison of the experimental and calculated correlation diagrams of Figure 4, the assignment of both groups of bands (each group corresponds to a signal in the spectra of **5**, **6**, and **16**) appears to be justified. The measured and calculated orbital energies of **5** and **16** agree remarkably well with the exception that the $1B_2(\pi_{SO_2})$ MO is predicted to lie somewhat high. The tentative assignment of bands 1 and 2 in the pe spectrum of **5** to the $B_1(\pi_{C=C})$ and $1B_2(\pi_{SO_2})$ MO's is based on the previous[22] finding that the C=C double bond exerts an inductive effect of about 0.2–0.3 eV on the $1B_2(\pi_{SO_2})$ MO. It must be stressed, however, that the exact ordering in **5** of the $B_1(\pi_{C=C})/1B_2(\pi_{SO_2})$ MO's (corresponding to bands 1 and 2) on the one hand and of the $1A_1(\sigma_{SO_2})/1B_1(\sigma_{SO_2})/1A_2(\pi_{SO_2})$ (corresponding to bands 3 to 5) on the other cannot be derived from experiment, mainly because the MO's in both groups of orbitals and therefore the corresponding bands of both signals are very close to one another. Nevertheless, the following discussion regarding the $\sigma\pi$ interaction in thiirene dioxides, specified above as interaction i, is independent of the exact ordering of levels within each group of orbitals in **5** and **6**.



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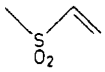

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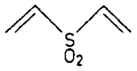

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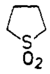

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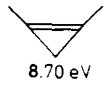
The energy of the $B_1(\pi_{C=C})$ MO in **5** prior to its interaction with the $1B_1(\sigma_{SO_2})$ MO is estimated from experimental data as follows. In agreement with MINDO/2 model calculations carried out with and without conjugative interruption between the double bond and the CH_2 group in 1,2-dimethylcyclopropene (**15**) and *cis*-1,2-dimethylethylene, the observed[18] energy difference (0.62 eV) between the π

MO's in both compounds (the corresponding ionization potentials are shown in **28** and **29** below) must be ascribed to



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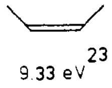

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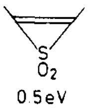
the hyperconjugative influence of the methylene group on the double bond of **15** (calculated energy difference between the π MO's of **15** and *cis*-1,2-dimethylethylene = 0.60 eV; calculated conjugative effect between the CH_2 and π MO in **15** = 0.67 eV). Based on these results the hyperconjugative effect ($\Rightarrow$) on the $B_1(\pi_{C=C})$ MO in **5** is assumed to be 0.62 eV. From previous pe results it was suggested that the inductive effect of the sulfone moiety exerted on adjacent π MO's is about 1.2 eV[8,22] and is rather independent on the nature of the π MO itself. In accordance with this result the inductive effect ($\rightarrow$) of the SO_2 group on the π MO in **5** is assumed to be 1.2 eV. In this manner the energy of the $B_1(\pi_{C=C})$ basis MO is found to be -10.52 eV. As shown in the theoretical part of Figure 4, the CNDO/S calculations predict nearly the same value (-10.46 eV) although the inductive contribution ($\rightarrow$ 0.60 eV) is underestimated and the hyperconjugative contribution ($\Rightarrow$ 0.95 eV) somewhat overestimated.

After introduction of this result into the correlation diagram of Figure 4 the presence of $B_1(\pi_{C=C})/1B_1(\sigma_{SO_2})$ hyperconjugation in **5** is obvious. This interaction amounts to about 0.5 eV. Recently the same sort of interaction (1.3 eV) was established for 2.5-di-*tert*-butylthiophene 1,1-dioxide (**11**).[8] The effects of the newly established π/σ_{SO_2} hyperconjugation in **5** and **11** are comparable in magnitude with the analogous π/CH_2 interactions in cyclopropenes (about 0.6 eV) and in cyclopentadiene (1.0 eV).[24] These effects are summarized in **30** to **33** below.



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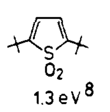

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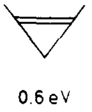

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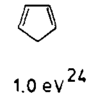

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As discussed above the pe spectrum of the monomethyl-substituted thiirene 1,1-dioxide (**6**) is very similar (two signals consisting of two and three bands, respectively) to the pe spectrum of the dimethyl-substituted counterpart **5**. However, all bands in the spectrum of **5** are shifted somewhat to lower ionization potentials relative to the corresponding bands in the spectrum of **5** (*cf.* Figure 5). The same trends are reproduced by the CNDO/S calculations. These results indicate that the methyl substituents in **5** and **6** influence *all* observable MO's. This result agrees with the previous[3] finding that the n MO of 2,3-di-*tert*-butylcyclopropenone (**4**) is strongly influenced by the presence of the two *tert*-butyl substituents. It must be concluded from these results that after their conjugative coupling, all relevant MO's of Figure 1 extend over the whole thiirene dioxide system. This result reminds us that the $1B_2(\pi_{SO_2})$ and $1A_1(\sigma_{SO_2})$ MO's (*cf.* Figure 1) also contain (as allowed by symmetry, but not shown in Figure 1) contributions from the ethylene part of the molecule.

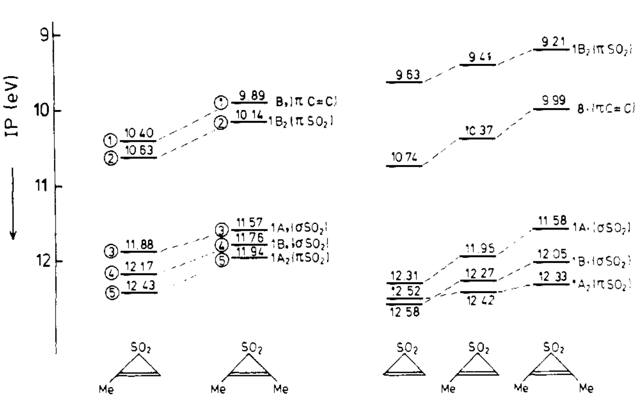
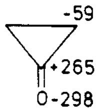


Figure 5. Measured and calculated correlation diagram for the highest occupied MO's of thiirene 1,1-dioxide (calculated only), 2-methylthiirene 1,1-dioxide, and 1,2-dimethylthiirene 1,1-dioxide. The numbers shown above the levels are vertical ionization potentials.

Charge Densities, Dipole Moments, and π Charge Transfer in Cyclic Unsaturated Sulfones and Ketones (Annulenones) in Conjunction with the Question of "Aromaticity" in These Systems. The CNDO/S charge density diagram (shown in **34** to **45** below; charges in 10^{-3} e) shows that the

34



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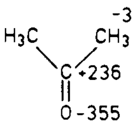

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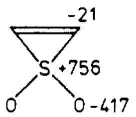

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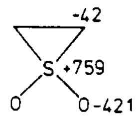

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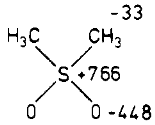

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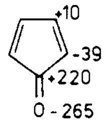

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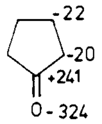

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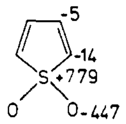

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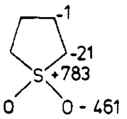

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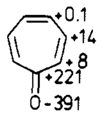

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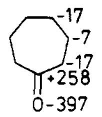

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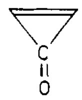
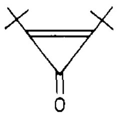
charge distribution of the SO_2 group in both the three- and five-membered rings (**37**, **38** and **42**, **43**, respectively) remains quite unaffected by the degree of unsaturation of the hydrocarbon chain. However, this is not true for the carbonyl compounds. The C=O group carries more negative charge in cyclopropenone (*cf.* **34**) and tropone (*cf.* **44**) and less negative charge in cyclopentadienone (*cf.* **40**) than in the saturated counterparts of these molecules (*cf.* **35**, **41**, and **45**, respectively). These results suggest that the C=O group accepts charge from the double bond in cyclopropenone and the hexatriene part of tropone but donates charge to the butadiene part in cyclopentadienone. These gross expectations are confirmed by calculating the π charge transfer (values are given in electrons in **46** to **52** below[25]) occur-



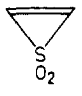
0.30e

46



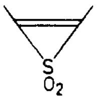
0.33e

47



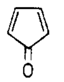
0.09e

48



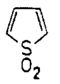
0.09e

49



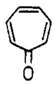
0.00e

50



0.00e

51



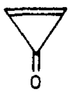
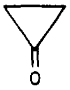
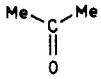
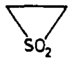
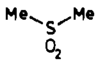
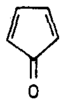
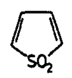
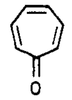
0.18e

52

ring from the unsaturated hydrocarbon unit to X (X = SO_2 and C=O) due to conjugation. This is achieved by considering the π charge distributions with and without interruption of conjugation. The greatest extent of π charge transfer is found for the cyclopropenones (*cf.* **46** and **47**), followed by tropone (*cf.* **52**). Charge transfer in the thiirene dioxides amounts to about one-third of the transfer predicted for the corresponding unsaturated ketones (*cf.* **46–49**). For both five-membered rings the π charge transfer is predicted to be nearly zero (*cf.* **50** and **51**). According to these results the cyclopropenone system is more developed in the direction of a cyclic 2π system than is the thiirene dioxide system. Whereas the tropone system obviously gains stability by transferring π charge to the carbonyl group (developing a partial 6π system), both the cyclopentadienone and thiophene dioxide system show no tendency for transferring any charge to the C=O or SO_2 groups. If we admit the calculated π charge transfer as a measure of the tendency of these systems to exhibit properties expected of an "aromatic" model *we then arrive at the following series: cyclopropenones > tropone > thiirene dioxides.* With cyclopentadienones and thiophene dioxides there is no transfer of charge to the carbonyl or sulfonyl group; a result which is at least in qualitative agreement with a crude picture of possible antiaromaticity effects in these systems. In connection with the transfer of π charge mentioned above it should be pointed out that, indeed, the molecular dipole moments in the ground state reflect the varied extent of π charge transfer (Table I) because the contributions due to the three-dimensional charge distribution (the sp and pd hybrid contributions) change much less than the contribution arising from the atomic point charges.

In conclusion, the results of this report have shown that the most important features of the electronic structure of cyclopropenones and thiirene dioxides (the inductive effect of X (X = C=O and SO_2) on the $\pi_{C=C}$ MO; the conjugative interactions between the $\pi_{C=C}$ MO and $\pi_{C=O}$ or σ_{SO_2} MO's; the conjugative interaction between the $\pi_{C=C}$ and $\pi^*_{C=O}$ or $\sigma^*_{SO_2}$ MO's) are very similar. What is apparently different between the two classes of compounds is probably not the nature of interactions between the double bond and X but only the strength of these interactions leading to the prediction that the thiirene dioxides are less shifted toward the "aromatic" model than their annulenone counterparts. It is felt from these results that extensive comparisons between the properties of unsaturated cyclic sulfones and ketones (annulenones) will be of great value in gaining new insight into the electronic nature of both classes of compounds.

Table I. Calculated Dipole Moments and Contributions to the Dipole Moments due to the Atomic Point Charges and the Three-Dimensional Charge Distribution Arising from the sp and pd Hybrids for Some Relevant Molecules

Molecule	Contributions to the dipole moment, D			
	Atomic point charges	sp	pd	Total
	4.12	1.40		5.52
	2.10	0.91		3.02
	2.50	1.09		3.59
	3.63	1.28	−0.38	4.53
	3.70	0.88	−0.33	4.25
	3.84	1.07	−0.20	4.71
	2.33	1.06		
	4.20	0.96	−0.34	4.82
	3.98	1.44		5.43

Acknowledgment. This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie. The calculations were carried out using the TR4 computer at the Rechenzentrum der Universität Marburg. We wish to thank Professor L. A. Carpino for generously providing us with samples of the thiirene 1,1-dioxides.

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(12) (a) P. H. Kasai, R. J. Myers, D. F. Eggers, Jr., and K. B. Wiberg, *J. Chem. Phys.*, **30**, 512 (1959). (b) After writing up this manuscript the correct structural data of 2,3-dimethylthiirene 1,1-dioxide (**5**) became available to us (we are very grateful to Professor Ammon, University of Maryland, for sending us these data prior to publication). The repetition of all calculations with the correct experimental geometry showed that all conclusions drawn, in the present paper, on the basis of the assumed geometry thereby remained unaffected.
(13) K. W. Schulte and A. Schweig, *Theor. Chim. Acta*, **33**, 19 (1974). All calculations are performed using the spd basis and the PSS1 parametrization scheme.
(14) Molecules **2** and **14** belong to the point group C_{2v}. All MO's are classi-

fied in terms of the symmetry species of this point group, of their respective π and σ nature as referred to the separated ethylene and SO_2 systems, and of the molecular parts (C═C or SO_2) where they are mostly localized. For the purpose of classification the substituted derivatives of **2**, **14**, and thiirane 1,1-dioxide are also treated to have C_{2v} symmetry.

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(25) It is interesting to note that the previously calculated MINDO/2 values (cyclopropenone = 0.29 e^3, 2,3-di-*tert*-butylcyclopropenone = 0.24 e^3, tropone = 0.15 e, and cyclopentadienone = 0.00 e) are in full accord with the present CNDO/S results.

Chemical Effects of Fission Recoils. II. Influence of Density and Oxygen Concentration on Product Formation in Ethylene

G. G. Meisels,* J. P. Gregory, A. A. Siddiqi,
J. P. Freeman, and W. C. Richardson

Contribution from the Chemonuclear Group, Department of Chemistry, University of Houston, Houston, Texas 77004. *Received June 27, 1974*

Abstract: The radiolysis of gaseous ethylene induced by recoils from fissioning U^{235} has been investigated in the density range 9×10^{-3} to 1.1×10^{-1} g cm^{-3} in the presence of small amounts of oxygen. The effect of density on acetylene yields was in accord with stabilization of initially formed excited molecules and/or ions, and with a change from differential to total energy loss of the fission recoil. From such studies the fission recoil range in ethylene was estimated to be 0.05 g cm^{-2}. The addition of oxygen was found to suppress the yields of *n*-butane and hexene-1 albeit only partially, but caused an increase in some other product yields. Plausible mechanisms consistent with reaction rate data are suggested and compared with conventional low-pressure ethylene radiolysis results.

One of the primary goals of radiation chemistry is the elucidation of principal processes occurring during the degradation of an energetic particle in a medium. The fission of the uranium atom has been employed only sparingly as a source but is interesting because the kinetic energy release of 170 MeV attendant to the fission process is well above that associated with conventional radiolytic sources, and because much of this energy is deposited in a very small volume.

The nuclear fission process has been studied extensively from a physical and theoretical point of view because of its obvious importance in nuclear power generation.[1] It is well known that the products of U^{235} fission induced by thermal neutron capture are distributed into two groups of light and heavy nuclei and that there is a wide distribution of recoil energies associated with each mass pair. The average energy per recoil is taken to be 85 MeV.[2] A summary of the nuclear properties of U^{235} is given in Table I.

Considerably less effort has been devoted to the study of the chemical changes induced by recoiling fission fragments in well defined chemical systems. Preliminary governmental and industrial studies generally focused on the use of the kinetic energy of recoiling fission products for the production of chemicals. Investigations of this kind were pioneered in the 1950's by Harteck and Dondes.[3] Moseley and Truswell[4] employed uranium-clad foil enriched with ^{235}U as a chemonuclear fuel element in the fission recoil radiolysis of N_2O. These investigations placed primary emphasis on developing a means of measuring energy deposition and the fixation of nitrogen in N_2–O_2 mixtures. At about the same time, a substantial effort along this line was initiated at the Brookhaven National Laboratory by Steinberg, Manowitz, and their coworkers.[5] A third effort in this direction was exerted by an industrial group under Air Force sponsorship, which was directed toward the synthesis of hydrazine by irradiation of ammonia.[6] All three groups employed, at least partially, circulating gas loops wherein the chemonuclear element was placed in the reactor and reactants were passed

Table I. Properties of ^{235}U Fission[a]

Total energy released in fission	190 MeV
Kinetic energy of fission recoils	160 MeV
Light fragment energy	103 MeV
Heavy fragment energy	57 MeV
Neutron energy	5 MeV
Prompt γ energy	5 MeV
Neutron capture γ energy	10 MeV
Decay γ	5 MeV
β radiation	5 MeV
Neutrons per fission	2.47
Light fragment mass	95 amu
Heavy fragment mass	140 amu
Light fragment charge	38 e
Heavy fragment charge	54 e

[a] Compiled from ref 2 and R. D. Evans, "The Atomic Nucleus," McGraw Hill, New York, N. Y., 1955.

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* Address correspondence to Department of Chemistry, University of Nebraska, Lincoln, Neb. 68508.

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