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COMPARATIVE *AB INITIO* AND VALENCE ELECTRON STUDY OF UNSATURATED 3-MEMBERED RING SYSTEMS. QUESTIONS OF CONJUGATIVE AND INDUCTIVE GROUP ABILITIES, OF AROMATICITY AND GEOMETRY

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Abstract—The method of conjugative interruption in conjunction with the CNDO/S and an *ab initio* method is applied to cyclopropene, cyclopropenone, cyclopropenthione, thiirene 1-oxide, and thiirene 1,1-dioxide. Thereby the orbital interactions between the π orbitals of the C=C and M(M=CH_2, C=O, C=S, S=O, and SO_2) subunits are quantitatively analyzed as well as their consequences as regards the conjugative and inductive abilities of M, the aromaticities, and geometries of this chemically important series of compounds. A detailed comparison of the CNDO/S and *ab initio* results is made. Both sorts of calculation yield surprisingly well concurring results. Where the results of both methods basically differ (as to the sign of the aromaticities, or the splitting pattern of two interacting orbitals) it can be traced back to the zero differential overlap approximation made for the valence electron procedure. In addition, the paper presents the first *ab initio* data on cyclopropenethione, thiirene 1-oxide, and thiirene 1,1-dioxide.

Chemists frequently use concepts such as inductive, conjugative, and steric abilities, orbital interactions, and aromaticity in a purely qualitative sense. To improve the situation we have been recently much concerned with studying a simple theoretical method for quantifying the effects associated with these concepts.[1–14] Preceding applications of the procedure have been done in the framework of valence electron methods. In this paper we proceed to apply an *ab initio* method. We compare in detail *ab initio* and valence electron results.

The methods are exemplified for the intriguing series


1


2


3


4


5

of molecules: cyclopropene (1), cyclopropenone (2), cyclopropenethione (3), thiirene 1-oxide (4), and thiirene 1,1-dioxide (5). These systems are quite relevant to aromaticity considerations. We present new aromaticity scales and define the positions of 1–5 on these scales. Furthermore, the relative inductive and conjugative abilities of the CH_2, C=O, C=S, S=O and SO_2 groups are evaluated. These data are backed by findings from pe studies[7] on the diphenyl derivatives 6–9[7a] of 1–4 and methyl and dimethylthiirene 1,1-dioxide (11 and 12).[7b]


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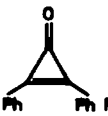
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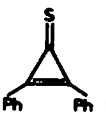
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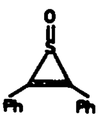
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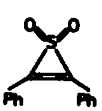
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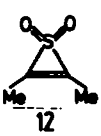
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The main valence electron procedure chosen is the CNDO/S method[15] extended to the second row.[16] The *ab initio* calculations are performed using the program POLYATOM.[17] Extended basis sets of double-ζ quality were used for H (3,1),[18,19] C, O (3,3,2,3:3,3)[20] and near double-ζ quality for S (4,4,3,3; 4,3,3).[21] In addition d polarization functions were included for S.[22] The geometry of 1,[33] 2,[24] 7,[25] 8,[26] 9[27] and 10[27] is experimentally known. For 5 the structural data of 12[27] were used and for 3 and 4 those of 8 and 9. The coordinate systems chosen are specified—where necessary—in Figures or Illustrations throughout the paper.

Orbital interactions

Let us start defining the various sorts of model interactions between M (CH_2, C=O, C=S, S=O and SO_2) and C=C that we have to take account of when interpreting the results of our approach. What we do first when applying our procedure is a full SCF calculation on any of the system 1 to 5 under study. Thereafter we interrupt π conjugation between C=C and M and perform a second "SCF" calculation. The orbital energies of both calculations differ. We define the energetic effect of M on the π orbital of the C=C unit in the interrupted case as the inductive effect of M (abbreviated throughout the paper as effect A). It summarizes all the influences that the charge polarized group M may exert through the intact σ system or directly through space on the $\pi_{C=C}$ orbital.

Passing over from the π interrupted to the π coupled case, orbitals of appropriate symmetry of both subunits start interacting to form molecular π orbitals. Simplifying here we distinguish three cases: interaction between the occupied $\pi_{C=C}$ orbital with occupied orbitals of M (leading to an energetic effect that is unfavorable and is designated throughout the paper as effect B), interaction between the filled $\pi_{C=C}$ orbital and vacant orbitals of M (leading to a gain in energy and abbreviated as effect C), and finally interaction between the vacant $\pi^*_{C=C}$ orbital and filled orbitals of M (which is energetically favorable again and is abbreviated as **effect D**).

The orbital energies in the conjugatively coupled and decoupled cases are arranged in interaction diagrams. The $\pi_{C=C}$ energy in the interrupted cases is indicative of the inductive effect of M when compared to the $\pi_{C=C}$ energy of a suitably chosen reference compound as ethylene or conjugatively decoupled cyclopropene (for a full discussion of this point see later sections. The energy changes that occur for the coupled orbitals when referenced against the uncoupled localized subunit orbitals directly indicate the strength of conjugative interactions.

As mentioned above energetic effects (affecting the total molecular energy) are connected with all three types of conjugative orbital interactions. Additionally, interactions of types C and D lead to a transfer of π charge from C=C to M or in the opposite direction, respectively. Both effects are readily available by considering the total energy and the π charge distribution in the coupled and decoupled cases. We refer in this paper to the energetic effects determined in this way as conjugation energy or aromaticity (for a full account on this point see a later chapter). If a sizable π charge transfer in either direction (from C=C to M or vice versa) occurs either geometrical changes (see a later chapter) or secondary changes in the orbital energies as a result of the π charge transfer (**effect E**) become possible. Some consequences of the latter effect will be discussed throughout the paper. It reminds us of the model character of our **effects A–E** which means that they are not strictly separable. They are interdependent. Nonetheless, it is our experience that their mutual influences are, as a rule, much smaller than the effects themselves. Therefore we are permitted to interpret calculated interaction diagrams in terms of **effects A–E** and in addition to believe in the reliability of the predicted conjugation energies (aromaticities) and π charge transfer data.

We now present the calculated interaction diagrams of **1–5** and analyse the orbital interactions in terms of conjugative **effects B–D** and their immediate consequences as π charge transfer and conjugation energy. The inductive influence of M (**effect A**) will be separately discussed in a subsequent chapter.

Cyclopropene (1) *and cyclopropenone* (2)

Figures 1 and 2 display the CNDO/S and *ab initio* orbital interaction diagram for cyclopropene (**1**) and cyclopropenone (**2**) (the solid bar across the C–C bonds in the structural formulas symbolizes conjugative interruption).[28–33]

For **1** we have to consider the (hyper)conjugative interactions between $\pi_{C=C}$ and π_{CH_2} (**effect B**) and additionally between $\pi_{C=C}$ and $\pi^*_{CH_2}$ (**effect C**, note that the star indicates as usual a vacant orbital). Due to the practically symmetric splitting between $\pi_{C=C}$ and π_{CH_2} and the tiny energy change of $\pi^*_{CH_2}$ in the CNDO/S case we must conclude that the stabilizing **effect C** (which determines at the same time the π charge transfer and the aromaticity of **1**) is rather unimportant for **1**. As judged from the $\pi^*_{CH_2}$ orbital energy change induced by conjugation in the *ab initio* case a bit more aromaticity and π charge transfer is to be anticipated for **1** (**effect C**). But the most prominent difference between the CNDO/S and *ab initio* calculations pertains to the interaction of the occupied orbitals (**effect B**). In the *ab initio* case the antibonding combination of $\pi_{C=C}$ and π_{CH_2} is much more destabilized than the bonding one is stabilized.

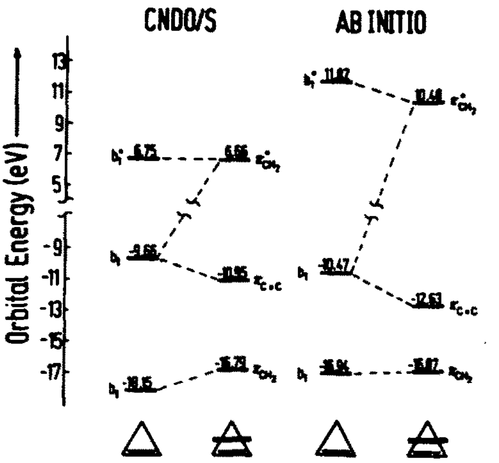


Fig. 1. CNDO/S and *ab initio* interaction diagrams of the respective orbitals of the C=C and CH₂ units of cyclopropene. The orbital energies prior to interaction are those obtained when the π conjugation between both subunits is interrupted. The interruption is symbolized by a dash across the C–C bonds. The highest occupied and lowest unoccupied (*) orbitals are classified in terms of their respective nature (π, σ or n), the subunit where they are localized, and the symmetry species of the point group that the molecule under study belongs to.

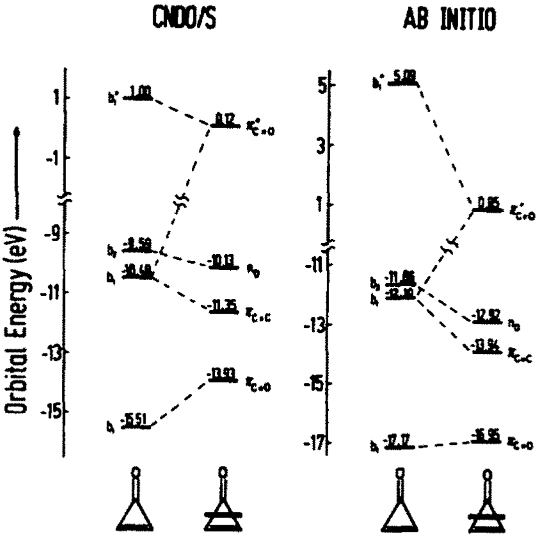


Fig. 2. CNDO/S and *ab initio* interaction diagrams of the respective orbitals of the C=C and C=O units of cyclopropenone. For further explanations, see caption to Fig. 1.

This behavior is clearly anticipated from overlap considerations. The CNDO/S method neglects overlap (zero differential overlap approximation) and therefore predicts necessarily and wrongly a symmetrical splitting pattern for two interacting occupied orbitals. The *ab initio* treatment is free from such a serious neglect and leads therefore to the correct splitting pattern.

Regarding the $\pi_{C=C}$, $\pi_{C=O}$ and $\pi^*_{C=O}$ localized orbitals of **2** the obtained interaction pattern is qualitatively similar as between the corresponding orbitals of **1**. Quantitative differences, however, occur as a consequence of the differing relative energies that these basis orbitals have in **2** as compared with **1**. Thus both the interactions between $\pi_{C=C}$ and $\pi_{C=O}$ (effect B) and between $\pi_{C=C}$ and $\pi^*_{C=O}$ (effect C) are much stronger leading us to expect **2** to be much more aromatic than **1** and experiencing a sizably higher π charge transfer from C=C to C=O than **1** from C=C to CH_2. In addition the extremely unsymmetrical $\pi_{C=C}/\pi_{C=O}$ splitting pattern is noteworthy for the *ab initio* case.

As mentioned above the π charge transfer from C=C to M is directly related to the stabilizing interaction between the $\pi_{C=C}$ and π_{M^*} orbitals and thus is a useful measure of the tendency of 3-membered ring systems to exhibit a partial (aromatic) cyclopropenylium structure. It can be further expected that the π charge transfer varies in accord with the amount of conjugation energy. These quantities along with the calculated pattern of atomic charges (printed on the atomic positions of the structural formulas shown), the dipole moment, and its change caused by conjugative decoupling are gathered in Fig. 3. In Fig. 3 as in any following figure of the same variety the first numbers give the CNDO/S values and the second ones (separated by semicolon) the *ab initio* counterparts.

The good agreement between the CNDO/S and the *ab initio* data in Fig. 3 is quite noteworthy. Note, however, the difference in magnitude and sign between the CNDO/S and *ab initio* conjugation energies.

The discrepancy is again a direct consequence of the different treatments of overlap by the CNDO/S and *ab initio* procedures. The valence electron methods (through their neglect of overlap) lead to symmetrical orbital splittings (see above) implying that an interaction between two occupied orbitals yields no net energetic effect. On the other hand the *ab initio* procedure takes full account of these effects so that finally the *ab initio* procedure counts all destabilizing (effect B) and stabilizing (effect C) effects. If the destabilizing interactions produce larger effects than the stabilizing ones the resulting conjugation energy is positive (as it is for **1** and **2** and also for **3**–**5** the case). Then lower positive values of the conjugation energy imply higher aromaticity. The CNDO/S method only counts the stabilizing interactions (effect C) and leads therefore necessarily to negative conjugation energies. The more these energies are negative the more the systems studied are aromatic.

Cyclopropenethione (3)

Figures 4 and 5 show the CNDO/S and *ab initio* interaction diagrams, both in an sp and spd basis, for cyclopropenethione (**3**).[34] As it can be seen, the sp and spd basis produce nearly the same orbital energies confirming that the d AOs on divalent sulfur atoms are negligible. What is further remarkable is the near degeneracy of the $\pi_{C=C}$ and $\pi_{C=S}$ orbitals resulting in a particularly strong interaction (effect B) and moreover due to the low energy of $\pi^*_{C=S}$ in an especially efficient stabilizing interaction (effect C). The latter type is responsible for more charge transfer and more aromaticity for **3** than for cyclopropenone (**2**). The latter data are collected in Fig. 6. The data of Fig. 6 further reveal that the major part of the dipole moment of cyclopropenthione is due to the π charge transfer and that the lowering in total energy due to inclusion of d orbitals on sulfur is rather low considering the corresponding lowering in thiophene to be −41.81 kcal/mol (CNDO/S) or −46.94 kcal/mol (*ab initio*). There is a general agreement in literature that the sulphur d orbitals in thiophene can be neglected.[35–37]

The n_S orbital in cyclopropenethione (**3**) just as the n_O orbital in cyclopropenone (**2**) (see Fig. 2) undergoes a rather dramatic shift upon switching on conjugation. At first brush, this is surprising since the conjugative status of the lone pair orbitals has not been changed by execut-

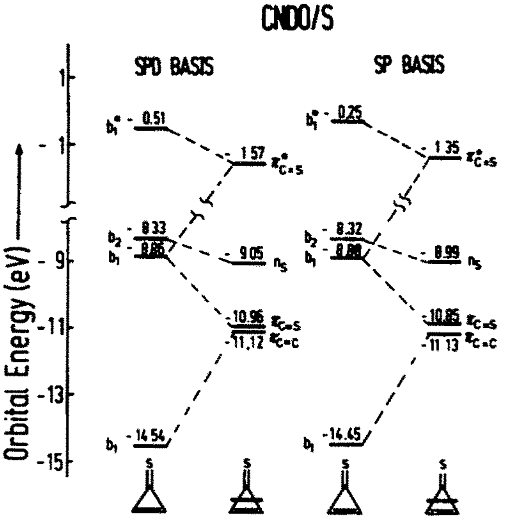
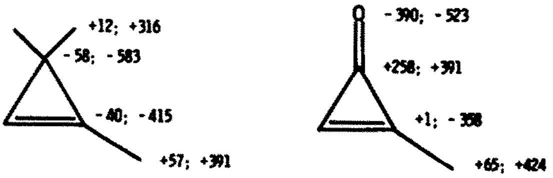


Fig. 4. CNDO/S interaction diagram of the respective orbitals of the C=C and C=S units of cyclopropenethione. The results of two calculations are presented, one performed using an spd basis (meaning that d orbitals on sulfur are considered) and the other using an sp basis. For further explanations, see caption to Fig. 1.



Dipole Moment	0.47 ; 0.34 (D)	4.74; 4.83 (D)
Δ Dipole Moment	0.16 ; 0.05 (D)	1.82; 2.49 (D)
π Charge Transfer	10 ; 60 (10^{-3}e)	230 ; 240 (10^{-3}e)
Conjugation Energy	-3.95 ; 78.63 (kcal/mol)	-42.45; 41.88 (kcal/mol)

Fig. 3. Electric (charge densities, printed at the respective atomic positions of the formulas shown; dipole moment; Δ dipole moment, i.e. the change in the dipole moment due to conjugation; π charge transfer) and energetic (conjugation energy) quantities obtained for cyclopropene and cyclopropenone using the CNDO/S and *ab initio* procedures. The CNDO/S results are always printed first (i.e. left to the semicolon), and the *ab initio* data follow (right to the semicolon).

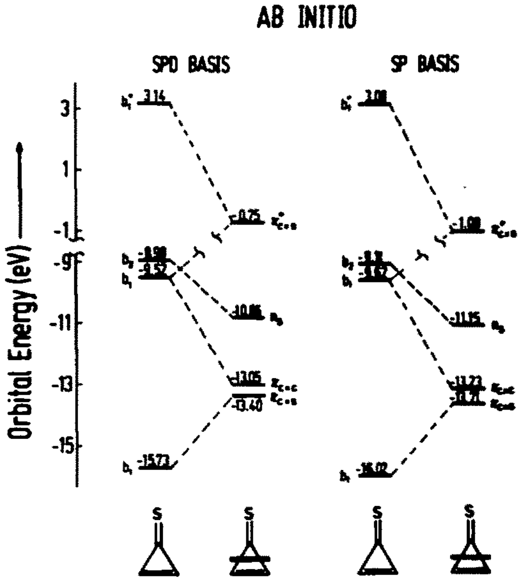


Fig. 5. *Ab initio* interaction diagram of the respective orbitals of the C=C and C=S units of cyclopropenethione. The results of two calculations are presented, one performed using an spd basis (meaning that the d orbitals on sulfur are included in the basis) and the other using an sp basis. For further explanations, see caption to Fig. 1.

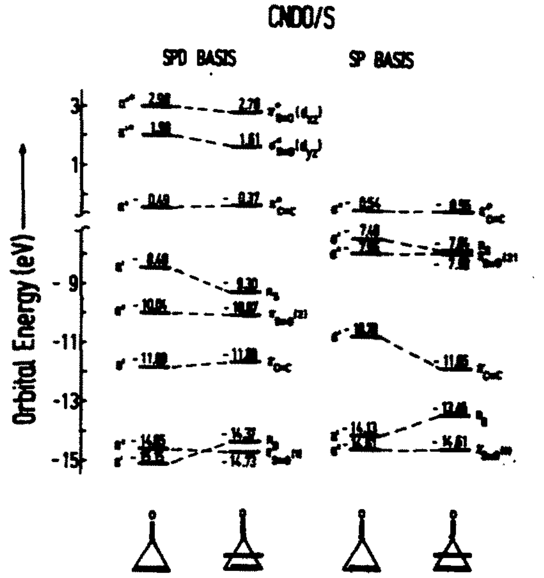


Fig. 7. CNDO/S interaction diagram of the respective orbitals of the C=C and S=O units of thiirene 1-oxide. The results of two calculations are presented, one performed using an spd basis and the other an sp basis. For further explanations, see caption to Figs. 1 and 9.

ing π conjugative manipulations. The nature of this effect is, however, easily understood. Due to the high π charge transfer (see Figs. 2 and 6) from C=C to M and the fact that the charge which accumulates on M mainly accumulates on the heteroatoms, the nuclear or core charge of O or S is more effectively screened so that the respective lone pair orbitals are pushed up. In a preceding section of this chapter we referred to this effect as secondary effect caused by charge transfer (effect E). It has been previously detected in a pe and nmr study of substituted cyclopentadienones.[6]

Thiirene 1-oxide (4)

Figure 7 presents the CNDO/S orbital interaction diagram, Fig. 8 the corresponding *ab initio* scheme, and Fig. 9 specifies the orbitals that are relevant for the interactions and the coordinate system which the orbitals are referred to.[38]

There are six S=O orbitals, three of symmetry a' and of the S=O σ type: the n_O and n_S "lone pairs" and the σ^*_{S-O} (d_{yz}) orbital which is practically a pure sulfur d orbital, and three belonging to the symmetry species a" and the S=O π type: the bonding $\pi_{S-O}(1)$ and antibonding $\pi_{S-O}(2)$ orbitals and the $\pi^*_{S-O}(d_{xz})$, again a practically pure sulfur d orbital. In addition we have the $\pi_{C=C}$ (symmetry a') and $\pi^*_{C=C}$ (symmetry a") orbitals. It is noteworthy that all four calculations (i.e. CNDO/S, *ab initio*, both in the sp and spd basis) predict the same sequence of orbitals.

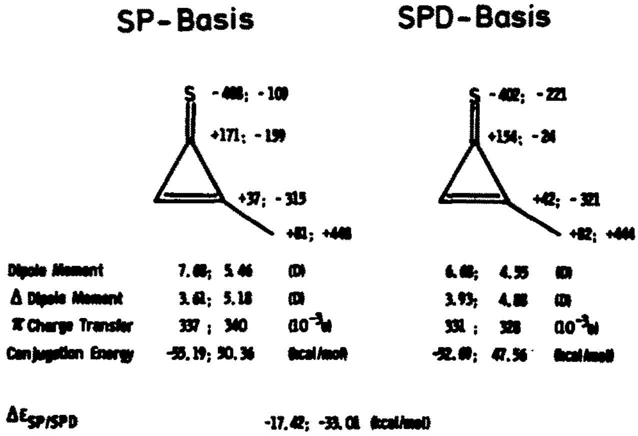


Fig. 6. Electric (charge densities, printed at the respective atomic positions of the formulas shown; dipole moment; Δ dipole moment, i.e. the change in the dipole moment due to conjugation; π charge transfer) and energetic (conjugation energy, $\Delta E_{sp,spd}$, i.e. the change in total energy due to inclusion of the sulfur d orbitals) quantities obtained for cyclopropenethione by use of the CNDO/S and the *ab initio* methods and an sp and an spd basis. The CNDO/S results are always printed first (i.e. left to the semicolon), and the *ab initio* data follow (right to the semicolon).

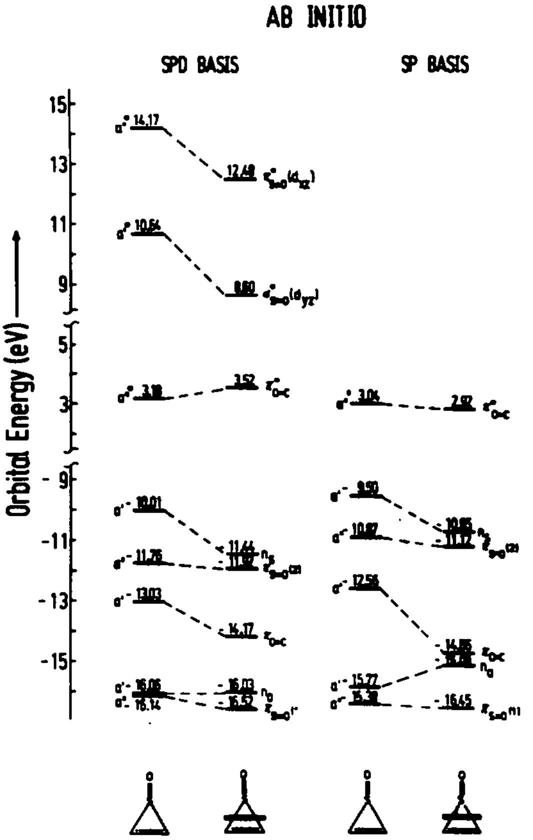


Fig. 8. *Ab initio* interaction diagram of the respective orbitals of the C=C and S=O units of thiirene 1-oxide. The results of an spd and an sp calculation are shown. For further explanations, see caption to Figs. 1 and 9.

Looking at the energies of the orbitals after interaction relative to the localized subunit orbitals we detect an interaction between the occupied a' orbitals. This interaction can be classified as hyperconjugative and is destabilizing (effect B). In addition, there is a stabilizing hyperconjugative contribution by mixing into the occupied a' orbitals the $\sigma^*_{S-O}(d_{yz})$ orbitals (effect C). The latter type is responsible for π charge transfer from C=C to S=O and part (presumably the major part, see below) of the stabilization of 4.

Moreover in this molecule, there is—different from the situation in 1–3—an interaction between the π^*_{C-C} orbital and π orbitals of S=O possible (effect D). This type of interaction can be considered as spiroconjugative[39–46] and leads also to aromatic stabilization and a π charge transfer, but now backwards from the S=O to C=C. The rather strong destabilization of the $\pi^*_{S-O}(d_{xz})$ orbital gives some indication that spiroconjugation may be involved to some extent in the bonding process. However, because of the low symmetry of 4 (i.e. C_s) we cannot separate both effects for this system. Such a separation becomes possible for thiirene 1,1-dioxide (5, *cf* the subsequent section of this chapter) and the results with regard to aromaticity will be discussed in full detail in a later chapter.

There are several indications that the sulfur d AOs play, contrary to the cyclopropenethione (3) case, an appreciable role in chemical bonding of thiirene 1-oxide (4). The orbital energies depend rather heavily on the d orbitals (see Fig. 7 and 8).

Accordingly the d orbital contributions to the orbitals are appreciable (see Fig. 9). In accord with these findings, the dipole moment caused by conjugation, just as the π charge transfer and conjugation energy or the lowering of the total energy are rather dependant upon the d orbitals on sulfur (Fig. 10).

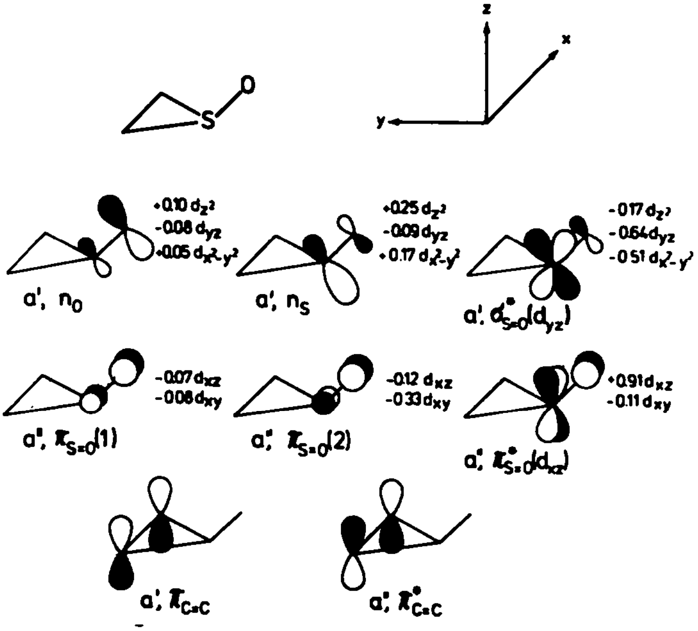


Fig. 9. Highest occupied and lowest unoccupied(*) orbitals obtained for the π decoupled C=C and S=O parts of thiirene 1-oxide. The orbitals are classified in terms of the symmetry species of the point group C_s, of their respective π, σ or n nature, and of the molecular units (C=C or S=O) where they are mostly localized. The vacant S=O orbitals are further characterized by adding the d orbital that mostly contributes to them and the two π_{S-O} orbitals are further specified by numbering them. The contributions (CNDO/S atomic orbital coefficients) of the respective d orbitals are explicitly given.

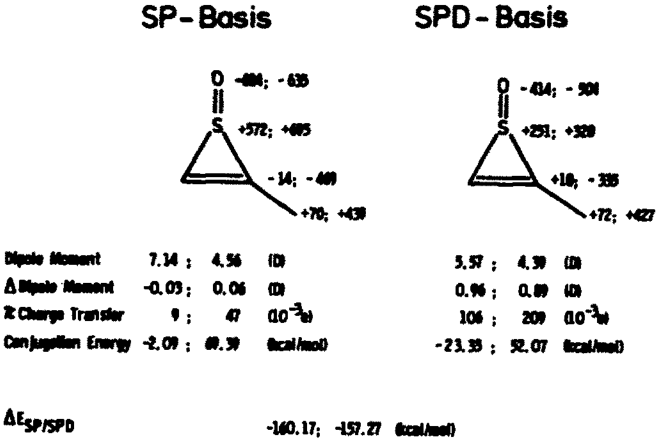


Fig. 10. Electric (charge densities, printed at the respective atomic positions of the formulas shown; dipole moment; Δ dipole moment, i.e. the change in the dipole moment due to conjugation; π charge transfer) and energetic (conjugative energy, change in the total energy due to inclusion of the d orbitals on sulfur) quantities obtained for thiirene 1-oxide using the CNDO/S and *ab initio* methods in the sp and spd basis. In all cases the numbers printed first (i.e. left of the semicolon) give CNDO/S results and the subsequent numbers (printed right to the semicolon) specify the *ab initio* values.

Thiirene 1,1-*dioxide* (5)

The orbital interactions in thiirene 1,1-dioxide and the implications with regard to aromaticity and charge transfer have been analysed in a preceding publication using the CNDO/S method.[7] We include here a modified CNDO/S interaction diagram (Fig. 11) in order to enable readers to compare it with the corresponding *ab initio* diagram (Fig. 12).[47] The modifications pertain to the geometry (now the experimental geometry of 12[27] is used) and to including the additional b_1, $\sigma_{SO_2}(1)$ orbital. This orbital and the other six relevant SO_2 orbitals together with the two C=C π orbitals are shown in Fig. 13. There are three πSO_2 orbitals and four σ SO_2 orbitals. Two of them, the a_2, $\pi^*_{SO_2}(d_{xz})$ and b_1, $\sigma^*_{SO_2}(d_{yz})$ are vacant and practically pure d orbitals.

Both diagrams (see Figs. 11 and 12) are in accord with appreciable hyperconjugative interactions within the b_1 manifold of orbitals (destabilizing effect B and stabilizing effect C, where the latter one is connected with a π charge transfer from C=C to SO_2).

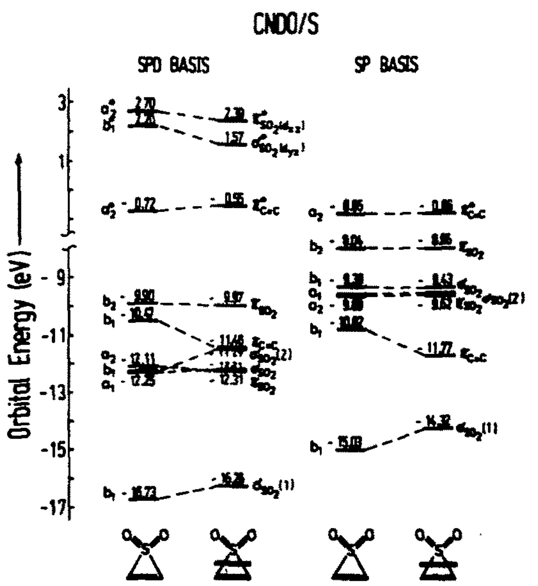


Fig. 11. CNDO/S interaction diagram of the respective orbitals of the C=C and SO_2 units of thiirene 1,1-dioxide, both in an spd and sp basis. For further explanations, see caption to Figs. 1 and 13.

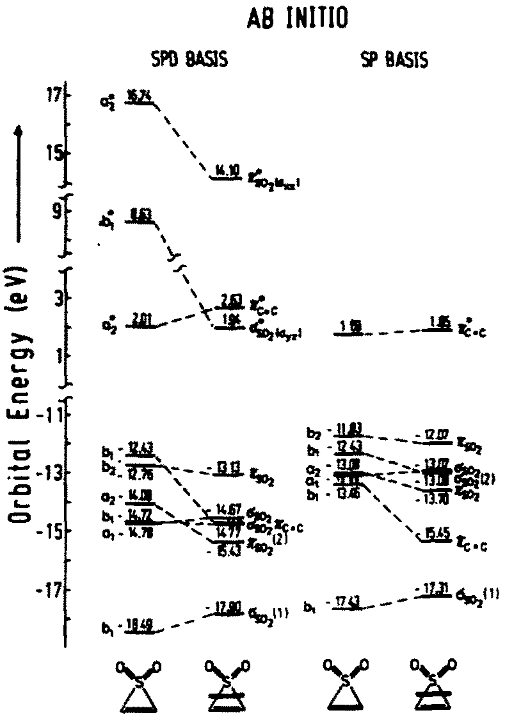


Fig. 12. *Ab initio* interaction diagram of the respective orbitals of the C=C and SO_2 units of thiirene 1,1-dioxide, both in an spd and an sp basis. For further explanations, see caption to Figs. 1 and 13.

Just as thiirene 1-oxide (4), thiirene 1,1-dioxide (5) meets the requirements for spiroconjugation. Moreover, the symmetry of 5 permits the spiroconjugative effect (effect D) to be calculated as separated from the aforementioned hyperconjugative effect (effects B plus C). To this end we make two selectively decoupled SCF calculations. In one of these calculations we interrupt con-

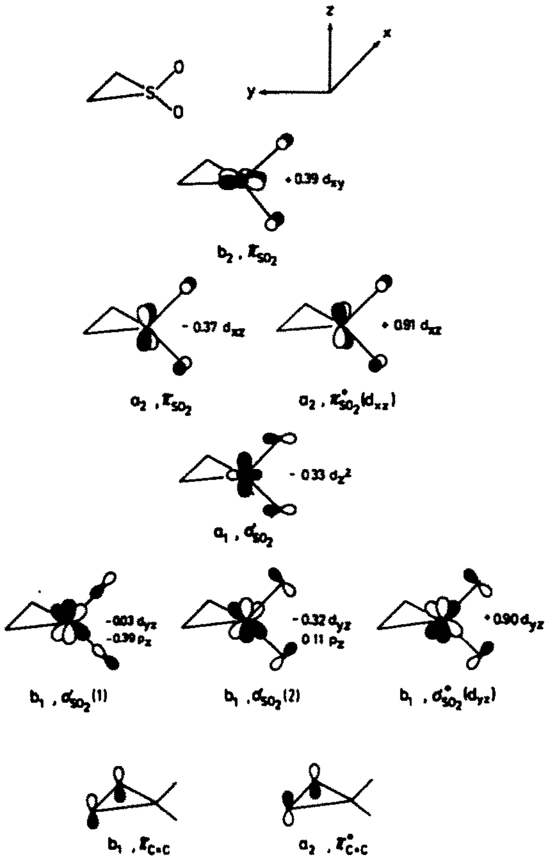


Fig. 13. Highest occupied and lowest unoccupied (*) orbitals obtained for the π decoupled C=C and SO_2 systems of thiirene 1,1-dioxide. The orbitals are classified in terms of the symmetry species of the point group C_{2v}, of their respective π or σ nature, and of the molecular units (C=C or SO_2) where they are localized. The vacant SO_2 orbitals are further characterized by adding the d orbital that mostly contributes to them and the two σ_{SO_2} orbitals of symmetry b_1 are made distinguishable by numbering them. The contributions (CNDO/S atomic orbital coefficients) of the respective d orbitals are explicitly given.

jugation between the two $2p_z$ atomic orbitals on C=C with the d_{xz} orbital on S and with the p_x orbitals on both oxygen atoms (note that the orbitals are specified with respect to the coordinate system shown in Fig. 13) thereby selectively excluding the spiroconjugative process. We can refer to these manipulations as a_2 decoupling. The results of such a calculation then reflect only hyperconjugative interactions. In the other calculation we selectively decouple conjugation between the p_z orbitals of C=C and the p_z and d_{yz} orbitals on sulfur and the s, p_y and p_z orbitals on the oxygen atoms, thereby retaining spiroconjugation but excluding hyperconjugation. We call this process b_1 decoupling.

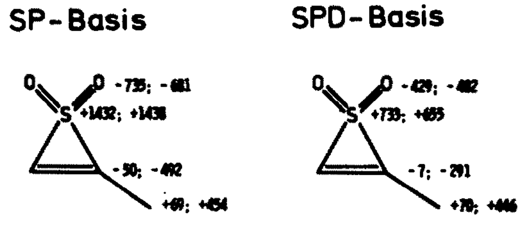
The main outcome of these calculations is that spiroconjugation (effect D) is negligible relative to hyperconjugation (effects B plus C). The result does not only mean that the orbital energies are little affected by spiroconjugation but also that the back transfer of charge from SO_2 to C=C as a result of this type of interaction is only tiny (for the data see Fig. 14) and that spiroconjugation energy (spiroaromaticity) is really small relative to the hyperconjugation energy (hyperaromaticity).

The influence of d orbitals on sulfur on the electronic structure of 5 is rather pronounced. This follows from the comparison of the orbital energies calculated with and without inclusion of the d orbitals on sulfur (see Fig. 11 and 12) and from the various quantities gathered in Fig. 14.

Aromaticity

In the foregoing chapter we listed the calculated conjugation energies (aromaticities) and the π charge transfer values[46] which are intimately connected with the aromaticities for the system 1–5. In this chapter we wish to discuss these values in more detail and to relate them with the corresponding quantities of a typical antiaromatic compound, cyclobutadiene, and on the other hand with benzene, a typically aromatic system.

Figure 15 displays the *ab initio* and CNDO/S conjugation energies. If all the levels are taken relative to the cyclobutadiene level, this diagram means that all other compounds studied (i.e. 1–5 and benzene) are more



	SP-Basis		SPD-Basis	
Dipole Moment	7.71 ; 5.83	(D)	5.54 ; 5.63	(D)
Δ Dipole Moment	-0.01 ; 0.78	(D)	0.74 ; 0.88	(D)
π Charge Transfer	1 ; 78	(10^{-3}e)	127 ; 225	(10^{-3}e)
Hyper π charge Transfer	6 ; 88	(10^{-3}e)	140 ; 251	(10^{-3}e)
Spiro π charge Transfer	7 ; -8	(10^{-3}e)	-13 ; -26	(10^{-3}e)
Conjugation Energy	-3.81 ; 60.67	(kcal/mol)	-33.44 ; 53.10	(kcal/mol)

$\Delta E_{SP/SPD}$ -320.38; 289.90 (kcal/mol)

Fig. 14. Electric (charge densities, printed at the respective atomic positions of the formulas shown; dipole moment; Δ dipole moment, i.e. the change in the dipole moment due to conjugation; π charge transfer; hyper π charge transfer, i.e. the contribution to the π charge transfer due to hyperconjugation; spiro π charge transfer, i.e. the contribution to the π charge transfer due to spiroconjugation) and energetic (conjugation energy, $\Delta E_{sp,spd}$, i.e. the change in the total energy due to the inclusion of the sulfur d orbitals) quantities obtained for thiirene 1,1-dioxide using the CNDO/S and *ab initio* procedures in an sp and spd basis. CNDO/S results are printed first (left to the semicolon) and the *ab initio* data follow (right to the semicolon).

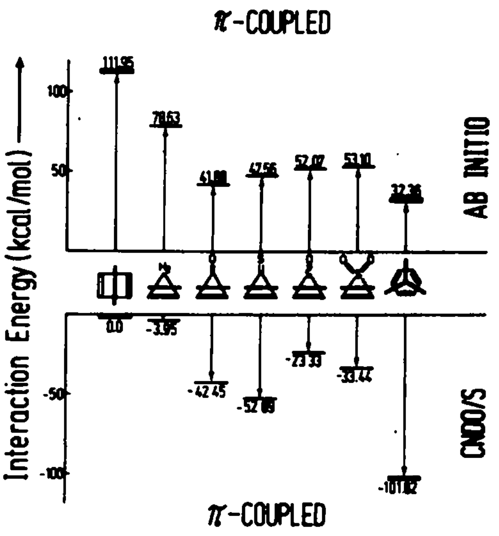


Fig. 15. Interaction energies (i.e. conjugation energies or aromaticities) between the respective π subunits of cyclobutadiene, cyclopropene, cyclopropenone, cyclopropenethione, thiirene 1-oxide, thiirene 1,1-dioxide, and benzene obtained using the *ab initio* and CNDO/S methods. The way of partitioning the π systems of the molecule under study into π subunits is indicated by solid bars.

aromatic than the reference system with benzene being the most aromatic one.

The gross features of the *ab initio* and CNDO/S diagrams are quite similar: cyclopropene is predicted to be the least aromatic system amongst the 3-membered rings and cyclopropenone (2) and cyclopropenethione (3) are indicated to be more aromatic than thiirene 1-oxide (4) and thiirene 1,1-dioxide (5).

Only the aromaticities of the similar (concerning their aromatic stabilisations) pairs of molecules 2 and 3 on one hand and of 4 and 5 on the other come out reversed in the *ab initio* case as to what is expected from the CNDO/S results. On the other hand both the aromaticity orders (as illustrated below) derived from the *ab initio* and

π Charge Transfer

CS > CO > SO_2 > SO > CH_2

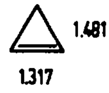
	CS	CO	SO_2	SO	CH_2	
CNDO/S	331	230	127	106	10	(10^{-3}e)
ab initio	329	240	225	209	60	(10^{-3}e)

CNDO/S charge transfer values concur and agree with the CNDO/S conjugation energy order (*cf* the lower part of Fig. 15). Therefore the CNDO/S energy order might be preferable.

According to the aromaticity orders defined above cyclopropenone is more aromatic than cyclopropene. This prediction is at variance with the magnetic criterion which leads to comparable aromaticities for both systems.[24] However in agreement with the predicted sizable aromaticity of cyclopropenone is a recent nmr measurement of the π charge transfer from C=C to C=O in *trans*-2,3-di-n-propylcyclopropenone.[49] The philosophy of this study is quite on line with our π charge transfer criterion of aromaticity. Thus there is some evidence that cyclopropenone is aromatic in its ground-state and that its aromaticity is not just a particular feature of its reactivity.[50]

Geometry

As shown in the preceding section the aromaticity of molecules 1–5 implies π charge transfer from C=C to M. As a result the C=C bond is weakened and the C=C bond elongates. Using the cut off method in connection with the MINDO/3 technique[51] and the Davidson–Fletcher–Powell method[52,53] the corresponding bond length changes (i.e. due to aromaticity) can be easily predicted (see 13–18 below). As the data indicate conjugation both elongates the C=C and C=O and C=S bonds and contracts the C–C (formally) single bonds connecting the C=C and M parts. These results are in full accord with the picture that charge is transferred from the bonding π C=C orbital into the antibonding $\pi^*_{C-O\,(C-S)}$ orbital and that due to the π interaction between C=C and M orbitals π bonding is superimposed on the C–C single bonds. Let us now investigate the C=C bond lengths of molecules 1–5 as an eventual indicator of the π conjugative process.



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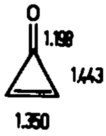

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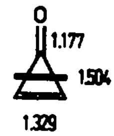

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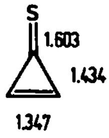

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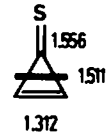

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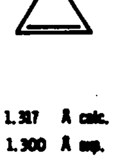
Since the experimental geometries of 3–5 are not known we consider instead the C=C bond lengths of the diphenyl derivatives 6–10. In this series only the experimental data of 6 are unknown. We estimate the "experimental" C=C length as follows. We calculate the C=C bond length of cyclopropene (1) applying a full geometry optimisation by use of the MINDO/3 method.[51–53] The C=C bond length obtained is 1.317 Å and thus 0.017 Å longer than the experimental length.[23] For 6 we calculate the C=C bond distance to be 1.353 Å. Correcting this value by 0.017 Å we finally arrive at 1.336 Å for the "experimental" C=C distance of 6 (for a summary of the data see 19 and 20 below).



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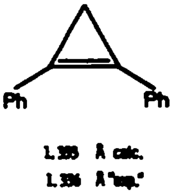

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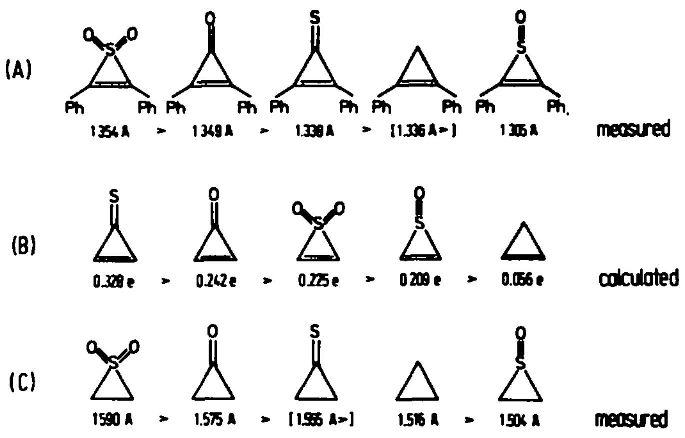


Fig. 16. 2,3-Diphenylthiirene 1,1-dioxide, 2,3-diphenylcyclopropenone, 2,3-diphenylcyclopropenethione, 1,2-diphenycyclopropene, and 2,3-diphenylthiirene 1-oxide in the order of decreasing C=C bond length (i.e. series A), cyclopropenethione, cyclopropenone, thiirene 1,1-dioxide, thiirene 1-oxide, and cyclopropene in the order of dropping π charge transfer from C=C to M (i.e. series B), and thiirane 1,1-dioxide, cyclopropanone, cyclopropanethione, cyclopropane, and thiirane 1-oxide in the order of decreasing C–C bond length (i.e. series C). Measured data set in brackets were estimated utilizing theoretical methods (see text for details).

In Fig. 16 molecules **6–10** are arranged in the order of decreasing measured C=C bond lengths (i.e. series A) and their unsubstituted counterparts **1–5** in the order of dropping π charge transfer. (i.e. series B). We see that both series do not at all correspond showing that the simple relationship between π charge transfer and the C=C bond length discussed above is not fulfilled. The clue to this discrepancies becomes immediately evident if we consider the series C of the saturated counterparts (i.e. cyclopropane (**21**),[54] cyclopropanone (**22**),[55] cyclopropanethione (**23**), thiirane 1-oxide (**24**),[56] and thiirane 1,1-dioxide (**25**)[57]) arranged in the order of decreasing $H_2C–CH_2$ bond lengths.[58–60] It is seen that arrangements A and C agree. The results means that the C=C bond lengths in the unsaturated molecules are predominantly determined by the σ system and only to a lesser and not determining extent by the π bonding processes. Therefore the C=C bond lengths in our series of unsaturated 3-membered ring systems cannot be used as a guide to the aromaticity of these systems. It is to be added that the experimental geometry of cyclopropanethione (**23**) is not known. Therefore its "experimental" C=C bond length was theoretically determined in the same way as described in detail for 1,2-diphenylcyclopropene (**6**) in the foregoing paragraph (this time the correction for the C–C bond is based on the deviation between calculation and measurement for cyclopropanone **22**, for all relevant data see **26** and **27** below).

21

22

23

24

25

1.520 Å calc.
1.575 Å exp.

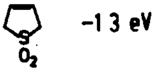
26

1.500 Å calc.
1.555 Å "exp."

27

Inductive effect of M(M = CH_2, C=O, C=S, S=O *and* SO_2

In a preceding chapter we defined the inductive effect of M (M = CH_2, C=O, C=S, S=O and SO_2) in the series of molecules **1–5** as the energetic influence that these groups exert on the $\pi_{C=C}$ orbital if the conjugation between C=C and M is interrupted. As reference the $\pi_{C=C}$ orbital energies of "fictional ethylene molecules" with the same C=C distance as in the respective three-membered ring counterparts were taken in the CNDO/S but not in the *ab initio* case (to save computer time). In view of our good experiences made previously with the prediction of inductive effects with the CNDO/2[61] procedure we additionally considered it here. The data obtained in this way for molecules **1–5** are with CNDO/S: 0.0 eV, −0.35 eV, −0.71 eV and −0.70 eV and with CNDO/2: 0.0 eV, −0.45 eV, −0.31 eV, −0.59 eV and −1.27 eV. Compared to these values and preceding experimental results (for some relevant measured effects see **29–38** below)[3,7,62–66] the *ab initio* data appear to be too high. The CNDO/2 data seem to be slightly preferable over the CNDO/S ones.



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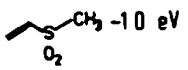

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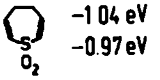

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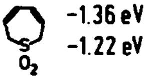

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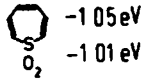

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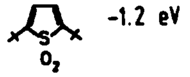

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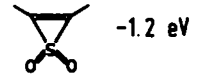

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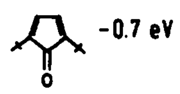

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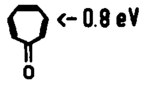

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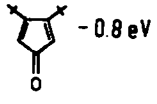

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CONCLUSION

In this paper we analyzed the various sorts of interactions and their consequences as π charge transfers, aromaticities, or geometries for the unsubstituted systems **1**–**5**. Furthermore we quantified the relative inductive and conjugative abilities of the CH_2, C=O, C=S, S=O and SO_2 groups in these systems. In a subsequent paper[7a] photoelectron spectroscopy is used to derive experimental information on the inductive and conjugative effects of these groupings in 1,2-diphenylcyclopropene, 2,3-diphenylcyclopropenone, 2,3-diphenylcyclopropenethione and 2,3-diphenylthiirene 1-oxide.

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