

# Photoelectron Spectra of 1,2-Diphenylcyclopropene, 2,3-Diphenylcyclopropenone, 2,3-Diphenylcyclopropenethione, 2,3-Diphenylthiirene 1-Oxide, and *cis*-Stilbene. An Experimental Verification of Conjugative and Inductive Interactions<sup>1</sup>

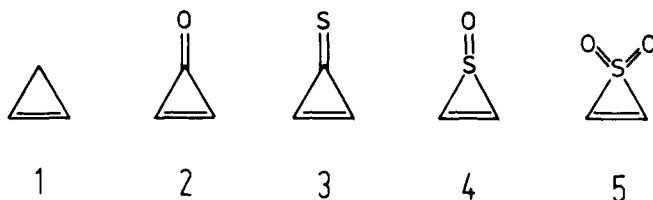
Claus Müller, Armin Schweig,\* and Hans Vermeer<sup>1</sup>

Contribution from the Fachbereich Physikalische Chemie, Universität Marburg, D-3550 Marburg/Lahn, West Germany. Received November 22, 1976

**Abstract:** The photoelectron spectra of the title compounds are interpreted and analyzed in terms of inductive and conjugative interactions between subunits M (CH<sub>2</sub>, C=O, C=S, S=O, and SO<sub>2</sub>) and PhC=CPh. Inductive and conjugative abilities of M derived in this way are compared to corresponding theoretical data obtained using the "cutoff" procedure. The same theoretical method is used to calculate aromaticities and  $\pi$  charge transfers. From these results and corresponding data derived from the unsubstituted species cyclopropene, cyclopropenone, cyclopropenethione, thiirene 1-oxide, as well as thiirene, 1,1-dioxide it is concluded that the diphenyl-substituted molecules are likely similar aromatic compounds as their parent systems are.

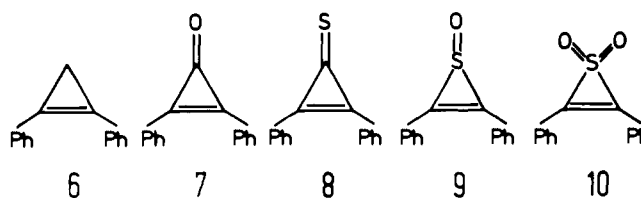
## Introduction

In a preceding paper<sup>2</sup> we analyzed the various sorts of interactions between M (CH<sub>2</sub>, C=O, C=S, S=O, and SO<sub>2</sub>) and the C=C unit in the intriguing series of molecules cyclopropene (1), cyclopropenone (2), cyclopropenethione (3), thiirene 1-oxide (4), and thiirene 1,1-dioxide (5). We further



considered the consequences (as, e.g.,  $\pi$  charge transfers, aromaticities, and geometries) of these interactions in terms of inductive and conjugative effects A-E defined as follows. Based on the "cutoff" procedure<sup>3-16</sup> we defined the energetic effect of M on the  $\pi$  orbital of the C=C unit in the  $\pi$  interrupted case as the inductive effect of M (i.e., effect A). Passing over from the  $\pi$  interrupted to the  $\pi$  coupled case orbitals of appropriate symmetry of both subunits start interacting to form molecular  $\pi$  orbitals. Simplifying here we distinguished three cases: interaction between the occupied  $\pi_{C=C}$  orbital with occupied orbitals of M (leading to an energetic effect that is unfavorable and designated 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 again is energetically favorable and is designated as effect D). Additionally, if a sizable  $\pi$  charge transfer in either direction (from C=C to M or vice versa) occurs due to effects C and D, respectively, secondary changes in the orbital energies as a result of the  $\pi$  charge transfer become possible (i.e., effect E).

Within the series of molecules 1-5 only 1 and 2 are existing compounds. Our present intention therefore is to seek experimental confirmation of the predicted inductive and conjugative abilities of M by use of the photoelectron (PE) spectra of the corresponding diphenyl derivatives 6-10. These molecules have a basic advantage over 1-5 insofar as the  $\pi$  systems of these molecules possess  $\pi$  orbitals which, for symmetry reasons, cannot couple with  $\pi$  orbitals of M so that their energy change reflects the purely inductive influence of M. Thus an approx-

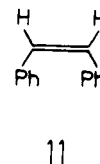


imate separation of the inductive from the conjugative effects can be achieved for 6-10 which is not possible for 1-5.

In order to estimate the modifications of the inductive and conjugative abilities of M caused by the phenyl substituents we will present theoretical results using the "cutoff" method for 6-10 (applied in the same way as for 1-5<sup>2</sup>) and compare them with the respective experimental data.

## Results and Discussion

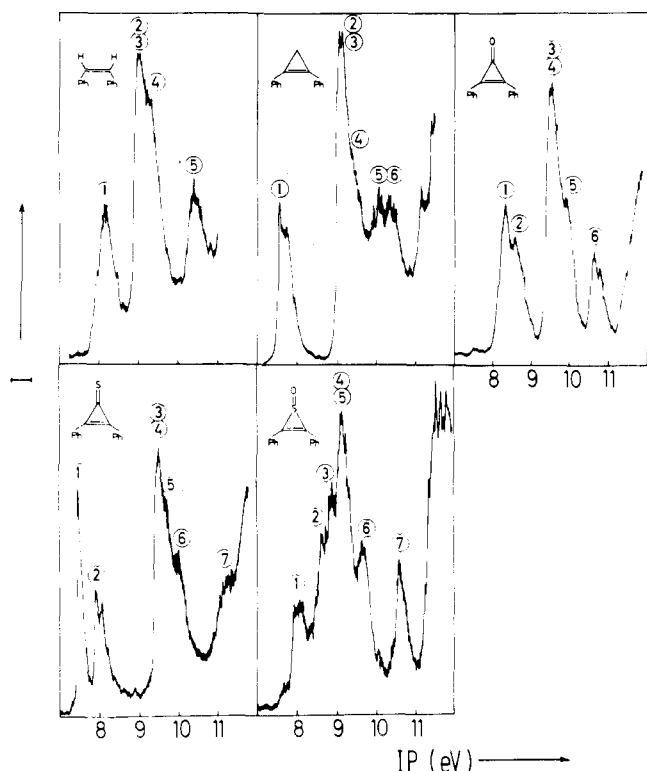
Figure 1 displays the photoelectron spectra of 1,2-diphenylcyclopropene (6), 2,3-diphenylcyclopropenone (7), 2,3-diphenylcyclopropenethione (8), 2,3-diphenylthiirene 1-oxide (9), and *cis*-stilbene (11).<sup>17</sup> Since 6-9 consist of PhC=CPh and M units the spectra of these compounds exhibit the band structure of 11 modified by inductive (effect A) and conju-



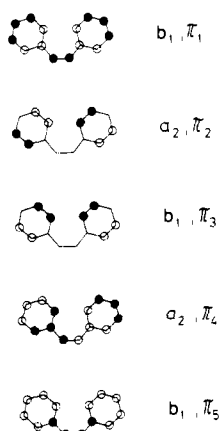
gative (effects B-E) interactions between the respective subunits and further modified by additional bands due to ionizations from other high-lying orbitals not involved in the  $\pi$  conjugation process.

***cis*-Stilbene (11).** The PE spectrum of 11 has been previously analyzed.<sup>18</sup> It shows three bands before the  $\sigma$  onset with the ratio of intensities 1.05:3:0.97. The corresponding ionizations 1-5 were assigned to the five  $\pi$  orbitals  $\pi_1$ - $\pi_5$  shown in Figure 2. These orbitals can be understood as linear combinations of C=C and  $\pi$  benzene orbitals.  $\pi_2$  and  $\pi_3$  are nearly degenerate.

*cis*-Stilbene is nonplanar with the phenyl rings rotated around the C-C bonds by 43.2°. In contrast to that the PhC=CPh part in 6-9 is planar. Therefore, before the influ-

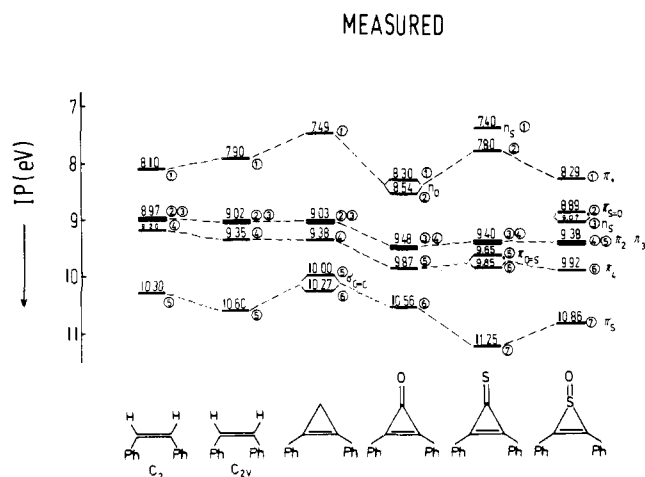


**Figure 1.** Photoelectron spectra of *cis*-stilbene, 1,2-diphenylcyclopropene, 2,3-diphenylcyclopropenone, 2,3-diphenylcyclopropenethione, and 2,3-diphenylthiirene 1-oxide. For the assignments and measured vertical ionization potentials, see Figure 3.

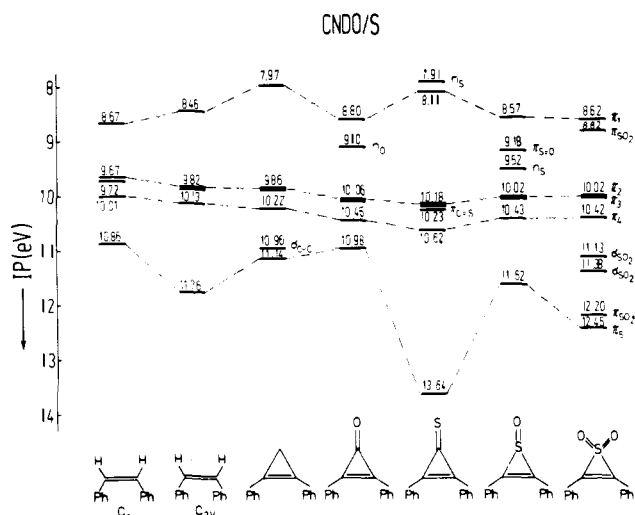


**Figure 2.** Highest occupied  $\pi$  orbitals of *cis*-stilbene. The orbitals are classified with respect to the symmetry species of point group  $C_{2v}$  and are further distinguished by numbering them (from 1 to 5 in order of decreasing energy).

ences of M on  $\pi_1$ – $\pi_5$  are to be quantified by comparing the ionizations of **11** with those of **6**–**9** we must correct the measured ionizations of **11** for the effects on  $\pi_1$ – $\pi_5$  that the change in geometry produces. The effects were estimated from MINDO/3,<sup>20</sup> CNDO/S,<sup>21,22</sup> and MNDO<sup>23</sup> calculations for the planar (symmetry  $C_{2v}$ ) and nonplanar (symmetry  $C_2$ ) forms of *cis*-stilbene. In accordance with what is expected on the orbital structures of  $\pi_1$ – $\pi_5$  all three valence electron methods agree in predicting 0.2 eV destabilization for  $\pi_1$  and 0.15 and 0.3 eV stabilization for  $\pi_4$  and  $\pi_5$ , respectively, and finally a tiny stabilization for the nearly degenerate  $\pi_2$  and  $\pi_3$  (0.05–0.1 eV) when passing over to the planar form. Both the measured (for the  $C_2$  form) and the corrected (belonging to the  $C_{2v}$  form) ionizations of *cis*-stilbene are gathered on the



**Figure 3.** Measured ionizations correlation diagram for *cis*-stilbene (point group  $C_2$ ), fictional planar *cis*-stilbene (point group  $C_{2v}$ ), 1,2-diphenylcyclopropene, 2,3-diphenylcyclopropenone, 2,3-diphenylcyclopropenethione, and 2,3-diphenylthiirene 1-oxide. The ionizations are labeled according to the designation of orbitals from which they arise. The numbers shown above the levels are vertical ionization potentials (in eV). The good agreement of the present diagram with the calculated Koopmans' ionizations correlation diagram of Figure 4 as well as the examination of Koopmans' ionizations by the configuration interaction (CI) method in ref 25–27 suggests that the present ionizations diagram may also be considered as an experimental correlation diagram for the highest occupied orbitals of the respective molecules. Consult text for details of estimating the ionization potentials for planar *cis*-stilbene.

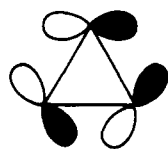


**Figure 4.** Calculated (using the CNDO/S method in conjunction with an spd basis) Koopmans' ionizations correlation diagram (identical with the orbital energy correlation diagram for the highest occupied orbitals) of *cis*-stilbene (point group  $C_2$ ), fictional planar *cis*-stilbene (point group  $C_{2v}$ ), 1,2-diphenylcyclopropene, 2,3-diphenylcyclopropenone, 2,3-diphenylcyclopropenethione, 2,3-diphenylthiirene 1-oxide, and 2,3-diphenylthiirene 1,1-dioxide. The numbers above the levels are vertical ionization potentials (or the negative of orbital energies in eV).

left-hand side of the measured ionization correlation diagram of Figure 3. Figure 4 displays the corresponding CNDO/S ionizations.<sup>24–27</sup> Our next problem is to relate the ionizations of **6**–**9** to the ionizations of the hypothetical planar form of *cis*-stilbene. Therefrom we can derive information about the interactions between  $\text{PhC}=\text{CPh}$  and M in **6**–**9**.

**1,2-Diphenylcyclopropene (6).** The  $\text{CH}_2$  part of **6** possesses neither lone pairs nor other high-lying  $\sigma$  orbitals. Therefore we would expect that, apart from the five  $\pi$  ionizations of the  $\text{PhC}=\text{CPh}$  unit, no additional ionizations that are charac-

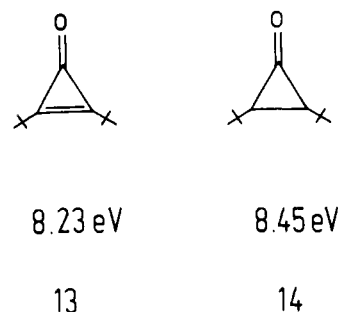
teristic for  $\text{CH}_2$  would arise in the  $\pi$  ionization region (i.e., the ionization region of *cis*-stilbene). Nonetheless, considering the PE spectrum of **6** and the ratio of intensities of its signals, there is one further ionization among the expected five  $\pi$  ionizations. This ionization is, however, understandable on the basis of the PE data of cyclopropene where the first  $\sigma$  ionization occurs at 10.89 eV.<sup>28</sup> This ionization is characteristic for the  $\sigma$  structure of the three-membered ring (for the orbital that is ionized see **12** below) and occurs for obvious reasons only in cyclopropene at such a high energy (note that, in cyclopropenone, the corresponding ionization is observed at 13.63 eV<sup>29</sup>).

 $\sigma_{\text{C-C}}$ **12**

The assignment of the six ionizations observed in the PE spectrum of **6** is based on the following arguments. From the structure of the five  $\pi$  orbitals shown in Figure 2, appreciable conjugative interactions can only be expected between  $\pi_{\text{CH}_2}$  and  $\pi^*_{\text{CH}_2}$  and  $\pi_1$  and  $\pi_5$ . From previous results<sup>2</sup> we have further to expect that the interaction with  $\pi_{\text{CH}_2}$  (effect B) predominates. Therefrom we would predict that, for **6**, the ionizations corresponding to  $\pi_1$  and  $\pi_5$  occur at lower energy than in planar *cis*-stilbene while the  $\pi_2$ - $\pi_4$  ionizations should be found at practically the same energy as in the fictional reference system. The three-membered ring  $\sigma$  ionization (symbolized as  $\sigma_{\text{C-C}}$  in Figure 3 and elsewhere) should occur at somewhat higher energy for **6** (because of interaction with  $\sigma_{\text{benzene}}$  orbitals) than for cyclopropene (**1**) (i.e., 10.89 eV, see above). All these expectations are met as Figure 3 shows. It must be stressed, however, that the sequence of the  $\sigma_{\text{C-C}}$  and  $\pi_5$  ionizations remains uncertain. The CNDO/S calculations place  $\sigma_{\text{C-C}}$  above  $\pi_5$ . However, qualitative arguments according to which the conjugative interaction between  $\pi_5$  and  $\pi_{\text{CH}_2}$  should be more efficient than between  $\pi_1$  and  $\pi_{\text{CH}_2}$  point to the opposite direction. Nonetheless the overall agreement between the measured (Figure 3) and calculated (Figure 4) ionizations for 1,2-diphenylcyclopropene and also relative to  $\text{C}_2$  and  $\text{C}_{2v}$  *cis*-stilbene is quite impressive.<sup>24-27</sup>

Most important, the results of Figure 3 (in full agreement with the theoretical results of Figure 4) indicate that the sum of conjugative (hyperconjugative) interactions between  $\pi_1$  and  $\pi_{\text{CH}_2}$  and  $\pi^*_{\text{CH}_2}$  (sum of effects B and C) is 0.4 eV. It is thus a bit smaller than the corresponding value (0.6 eV)<sup>9</sup> previously derived for 1,2-dimethylcyclopropene in accordance with what is expected on the relative energies of the  $\pi_{\text{C=C}}$  orbital of 1,2-dimethylcyclopropene and  $\pi_1$  of **6**.

**2,3-Diphenylcyclopropenone (7).** The band structure of the PE spectrum of **7** is very similar to that of *cis*-stilbene with one additional band in the range of the first signal. The intensity ratio of the three signals is 2.09:3:0.98. From our previous experience<sup>8</sup> with the oxygen lone pair ( $n_{\text{O}}$ ) ionizations for 2,3-di-*tert*-butylcyclopropenone and *trans*-2,3-di-*tert*-butylcyclopropanone (**13** and **14** below) one of the first two bands in the PE spectrum of **7** must be assigned to the  $n_{\text{O}}$  orbital. The CNDO/S calculations place  $\pi_1$  above  $n_{\text{O}}$  but CNDO/S CI calculations made in order to estimate the Koopmans defects suggest the reversed sequence.<sup>24-27</sup> Irrespective of the exact ordering, however, an  $n_{\text{O}}$  ionization around 8.30 eV reveals that the  $n_{\text{O}}$  orbital in the three-membered ring systems is drastically destabilized with respect to the same orbital in aliphatic ketones (e.g., 9.71 eV<sup>30</sup> in acetone and 9.21 eV<sup>31</sup> in methyl *tert*-butyl ketone). The observed destabilization is partly due



8.23 eV

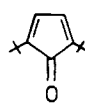
8.45 eV

**13****14**

to a strong interaction with the  $\sigma$  system of the ring and partly a consequence of the secondary  $\pi$  charge transfer from  $\text{PhC=CPh}$  to  $\text{C=O}$  (effect E).

The location of the  $\pi_1$  ionization for **7** relative to the same ionization for planar *cis*-stilbene (Figure 3) indicates that, for **7**, the stabilizing influences exerted by  $\text{C=O}$  on  $\pi_1$  (i.e., effects A, C, D) predominate. For symmetry reasons the  $\pi_2$  and  $\pi_4$  orbitals can only experience inductive stabilizations so that we can use their energy changes as a measure of the pure inductive effect (effect A). Since, however, the  $\pi_1$ - $\pi_5$  orbitals (Figure 2) lead to rather different electronic distributions the inductive influences of  $\text{C=O}$  on  $\pi_1$ - $\pi_5$  might differ to a certain extent. This is indeed the case as the results of CNDO/2,<sup>32</sup> CNDO/S, MINDO/3, and MNDO calculations with and without conjugative interruption indicate. All methods applied agree that the inductive stabilizations of  $\pi_1$  and  $\pi_5$  are the largest ones. As compared to that value the  $\pi_4$  stabilization amounts to 70% and the  $\pi_2$  and  $\pi_3$  stabilization to 60%. It is further interesting to mention that the found graduation of effects is valid for all other groups studied.

If we modify the measured (Figure 3) inductive effects for  $\pi_2$  and  $\pi_4$  according to the aforementioned orbital sensitivity scale we arrive at an inductive stabilization of -0.75 eV for  $\pi_1$  and  $\pi_5$ . This value is in good agreement with the inductive effects of  $\text{C=O}$  in substituted cyclopentadienones<sup>8</sup> and tropone<sup>5</sup> (cf. **15**-**17**). Relying on this inductive stabilization (-0.75 eV),



-0.7 eV

**15**

&lt;-0.8 eV

**16**

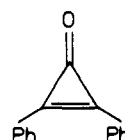
-0.8 eV

**17**

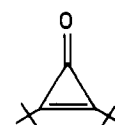
the sum of stabilizing (interaction of  $\pi_1$  with  $\pi^*_{\text{C=O}}$ , i.e., effect C) and destabilizing (interaction of  $\pi_1$  with  $\pi_{\text{C=O}}$ , i.e., effect B) conjugative interactions does not exceed 0.1-0.35 eV (depending on band 1 or 2 in the PE spectrum of **7** being assigned to  $\pi_1$ ). The derived value is within the limits of findings<sup>9</sup> for other cyclopropenone systems (cf. **18** and **20** with **19** below; for a more detailed discussion, however, see below).



0.4 eV

**18**

0.1-0.35 eV

**19**

0.0 eV

**20**

**2,3-Diphenylcyclopropenethione (8).** At first glance the PE spectrum of **8** appears to be quite different from the reference

spectrum of *cis*-stilbene (Figure 1). It exhibits three signals with an intensity ratio of 1:1.02:4.05. In addition there is a fourth signal in the onset of the  $\sigma$  continuum.

These observed differences are due to the higher energies of  $\pi_{C=S}$  and  $n_S$  orbitals than of their oxygen counterparts (e.g.,  $\pi_{C=O}$  of acetone at 12.62 eV,<sup>30</sup>  $\pi_{C=S}$  of thioacetone at 10.46 eV,<sup>34</sup>  $n_O$  of acetone at 9.72 eV<sup>30</sup> and  $n_S$  of thioacetone at 8.60 eV<sup>34</sup>). In addition, the  $n_S$  ionization of **8** is (in analogy to the respective oxygen cases) expected to occur at considerably lower energy than in aliphatic compounds (owing to  $\sigma$  interactions and  $\pi$  charge transfer from  $\text{PhC}=\text{CPh}$  to  $\text{C}=\text{S}$ ).

Keeping these facts in mind the interpretation of the PE spectrum of **8** is possible. Unambiguously, both from the shape of band 1 and the vibrational fine structure of band 2 (1291  $\text{cm}^{-1}$ ,  $\text{C}=\text{C}$  vibration in the molecule 1785  $\text{cm}^{-1}$ <sup>35</sup>) bands 1 and 2 must be assigned to the  $n_S$  and  $\pi_1$  orbitals, respectively. The relative intensity of the second signal indicates that the  $\pi_{C=S}$  ionization is additionally located in the  $\pi_2$ - $\pi_4$  ionization region. The sequence of  $\pi_{C=S}$  and  $\pi_4$  ionizations cannot be inferred from the experimental data.

Following the same procedure as described above for 2,3-diphenylcyclopropenone (**7**) we derive, from the observed changes in the  $\pi_2$  and  $\pi_3$  ionization energies relative to those of planar *cis*-stilbene, an inductive effect of  $\text{C}=\text{S}$  on  $\pi_1$  of  $-0.6$  eV (effect A). With this inductive effect we estimate, from the  $\pi_1$  ionization energy of **8** for the sum of stabilizing (interaction with  $\pi^*_{C=S}$ , effect C) and destabilizing (interaction with  $\pi_{C=S}$ , effect B) conjugative contributions, a value of 0.7 eV.

It is worth mentioning that all assignments and conclusions derived above for **7** and **8** are additionally corroborated by the quite impressive agreement between the calculated (Figure 4) and measured (Figure 3) ionization energies for these molecules.<sup>24-27</sup>

**2,3-Diphenylthiirene 1-Oxide (9).** The PE spectrum of **9** (Figure 1) exhibits two additional bands (2 and 3) in the  $\pi_1$ - $\pi_5$  ionization region. We assign these bands, relying on the CNDO/S calculations of Figure 4, to the  $n_S$  and  $\pi_{S=O}$  orbitals.<sup>2</sup> This assignment gets support from the shape of the second intense signal (comprising bands 2-6) in the PE spectrum of **9** (Figure 1) where—as it must be expected from the near degeneracy of the  $\pi_2$  and  $\pi_3$  orbitals (cf. Figure 2)—bands 4 and 5 form the most intense peak and therefore have to be assigned to these orbitals.

According to a preceding analysis<sup>2</sup> of orbital interactions for thiirene 1-oxide we would essentially expect here conjugative interactions between  $\pi_1$  and  $\pi_5$  and  $n_S$  on one hand and  $\pi_4$  and  $\pi_{S=O}$  on the other.  $\pi_2$  and  $\pi_3$  are then appropriate for estimating the inductive influence of  $\text{S}=\text{O}$ . From the changes of the corresponding ionizations (relative to the corresponding ionizations of planar *cis*-stilbene) we evaluate for the inductive stabilizations of  $\pi_1$  and  $\pi_5$   $-0.65$  eV. Based on this inductive effect the conjugative interactions (i.e., the sum of effects B and C) amounts to 0.25 eV for  $\pi_1$ .

**2,3-Diphenylthiirene 1,1-Dioxide (10).** We did not succeed in recording the PE spectrum of **10** since this molecule quantitatively decomposed into diphenylacetylene during the evaporation process. This is in agreement with mass spectral findings.<sup>36</sup>

**Comparison between Calculated and Experimental Results and Conclusion.** Figure 5 gathers the calculated CNDO/2 inductive effects of M on  $\pi_1$  (effect A), the corresponding experimental quantities as derived in the preceding PE spectral study, the calculated CNDO/S conjugative effect of M on  $\pi_1$  (effects B plus C), and the corresponding experimental quantities as again obtained from the preceding PE spectral data. In both cases, the calculated and experimental results are—in view of the various approximations involved—in a satisfactory agreement.<sup>37</sup>

(A) inductive effect	calc., in eV	0.02	-0.35	-0.23	-0.46	-0.95
(B) inductive effect	exp., in eV	0.0	-0.75	-0.6	-0.65	-
(C) conjugative effect	calc., in eV	0.4	0.04	0.5	0.1	0.06
(D) conjugative effect	exp., in eV	0.4	0.1-0.35	0.7	0.25	-

**Figure 5.** Calculated CNDO/2 inductive (A) and CNDO/S conjugative (C) effects of M (M =  $\text{CH}_2$ ,  $\text{C}=\text{O}$ ,  $\text{C}=\text{S}$ ,  $\text{S}=\text{O}$ , and  $\text{SO}_2$ ) on the  $\pi_1$  orbital of the  $\text{PhC}=\text{CPh}$  subunit of 1,2-diphenylcyclopropene, 2,3-diphenylcyclopropenone, 2,3-diphenylcyclopropenethione, 2,3-diphenylthiirene 1-oxide, and 2,3-diphenylthiirene 1,1-dioxide and the corresponding experimental (except for thiirene 1,1-dioxide) effects (B and D) as derived by PE spectroscopy.

We further note from the data of Figure 5 that the inductive effects of M on  $\pi_1$  are quite similar to the corresponding effects of M on  $\pi_{C=C}$  in the parent compounds **1-5**.<sup>2</sup> This result confirms our previous experience that the inductive effects of groupings M are surprisingly independent of the particular  $\pi$  orbital that they exert their effect on. However, we realize from Figure 5 and previous results<sup>2</sup> that the conjugative influence of M on  $\pi_1$  is quite different from the corresponding influence of M on  $\pi_{C=C}$  in the parent compounds **1-5**. This outcome is not surprising because the  $\pi$  orbital structure of  $\text{PhC}=\text{CPh}$  (cf. Figure 2; remember particularly that there are two  $\pi$  orbitals,  $\pi_1$  and  $\pi_5$ , that can conjugate with  $\pi$  orbitals of M) and the energies of  $\pi_1$  and  $\pi_5$  relative to the relevant orbitals of M are quite different from what is calculated for the unsubstituted molecules **1-5**. Nonetheless, the calculations further show that the amounts of  $\pi$  charge transfers in **6-10**<sup>38</sup> are very similar to those in **1-5**.<sup>2</sup> The same is found for the aromaticities of both series of compounds (i.e., **1-5**<sup>2</sup> and **6-10**<sup>39</sup>). From all that we have to conclude that the diphenyl substituted molecules **6-10** are likely similar aromatic compounds as their parent systems **1-5** are.

**Acknowledgment.** This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie. The calculations were carried out using the TR 440 computer at the Rechenzentrum der Universität Marburg and the IBM 370/168 computer at the Rechenzentrum der TH Darmstadt. Samples of 1,2-diphenylcyclopropene (**6**), 2,3-diphenylcyclopropenone (**7**), 2,3-diphenylcyclopropenethione (**8**), 2,3-diphenylthiirene 1-oxide (**9**), and 2,3-diphenylthiirene 1,1-dioxide (**10**) have been provided by M. A. Bastide and R. A. Fiato, Gainesville, Fla. (**6**), F. Dunkelblum, Jerusalem (**7**), J. W. Lown, Edmonton (**8**), and L. A. Carpino, Amherst, Mass. (**9** and **10**), respectively.

## References and Notes

- (1) Part 70 of "Theory and Application of Photoelectron Spectroscopy". Part 69: C. Müller, A. Schweig, M. P. Cava, and M. V. Lakshmikantham, *J. Am. Chem. Soc.*, **98**, 7187 (1976).
- (2) H.-L. Hase, C. Müller, and A. Schweig, *Tetrahedron*, **34**, 2983 (1978).
- (3) N. C. Baird, *Theor. Chim. Acta*, **16**, 239 (1970).
- (4) H.-L. Hase and A. Schweig, *Tetrahedron*, **29**, 1759 (1973).
- (5) C. Müller, A. Schweig, and H. Vermeer, *Angew. Chem.*, **86**, 275 (1974); *Angew. Chem., Int. Ed. Engl.*, **13**, 273 (1974).
- (6) H. Schmidt, A. Schweig, R. W. Hoffmann, and H. Kurz, *Tetrahedron Lett.*, 1953 (1974).
- (7) H. Schmidt, A. Schweig, and A. Krebs, *Tetrahedron Lett.*, 1471 (1974).
- (8) W. Schäfer, A. Schweig, G. Maier, T. Sayrac, and J. K. Crandall, *Tetrahedron Lett.*, 1213 (1974).
- (9) C. Müller, A. Schweig, and H. Vermeer, *J. Am. Chem. Soc.*, **97**, 982 (1975).
- (10) H. Schmidt, A. Schweig, F. Mathey, and G. Müller, *Tetrahedron*, **31**, 1287 (1975).
- (11) W. Schäfer, A. Schweig, and F. Mathey, *J. Am. Chem. Soc.*, **98**, 407 (1976).
- (12) W. Schäfer, A. Schweig, K. Dimroth, and H. Kanter, *J. Am. Chem. Soc.*, **98**, 4410 (1976).
- (13) H. Schmidt and A. Schweig, *Z. Naturforsch. A*, **31**, 215 (1976).
- (14) H. Schmidt, A. Schweig, and H. Vermeer, *J. Mol. Struct.*, **37**, 93 (1977).
- (15) H. Schmidt, A. Schweig, A. G. Anastassiou, and J. C. Wetzel, *Tetrahedron*,

- 32, 2239 (1976).
- (16) C. Müller, A. Schweig, M. P. Cava, and M. V. Lashmikantham, *J. Am. Chem. Soc.*, **98**, 7187 (1976).
- (17) The photoelectron spectra have been recorded on a Perkin-Elmer PS-16 spectrometer.
- (18) T. Kobayashi, K. Yokota, and S. Nagakura, *Bull. Chem. Soc. Jpn.*, **48**, 412 (1975).
- (19) M. Traettenberg and E. B. Frantsen, *J. Mol. Struct.*, **26**, 69 (1975).
- (20) R. C. Bingham, M. J. S. Dewar, and D. H. Lo, *J. Am. Chem. Soc.*, **97**, 1285 (1975).
- (21) H. H. Jaffé, *Acc. Chem. Res.*, **2**, 136 (1969), and references cited therein.
- (22) K.-W. Schulte and A. Schweig, *Theor. Chim. Acta*, **33**, 19 (1974).
- (23) M. J. S. Dewar and W. Thiel, *J. Am. Chem. Soc.*, **99**, 4899 (1977).
- (24) The ionization levels depicted in Figure 4 are Koopmans' ionization levels relying on Koopmans' theorem: T. Koopmans, *Physica (Utrecht)*, **1**, 104 (1934). We checked the Koopmans' results using a recently developed CI approach<sup>25-27</sup> in two cases: for 2,3-diphenylcyclopropenone (**7**) and 2,3-diphenylthiirene 1-oxide (**9**). Both cases merit special attention because of the closely spaced Koopmans' lone pair and  $\pi$  ionizations ( $\pi_1$  and  $n_0$  for **7** and  $\pi_{S=O}$  and  $n_S$  for **9**). For these ionizations we find  $n_0$  followed by  $\pi_1$  (i.e., sequence reversal) for **7** and  $\pi_{S=O}$  followed by  $n_S$  for **9** (i.e., no sequence reversal).
- (25) G. Lauer, K.-W. Schulte, and A. Schweig, *Chem. Phys. Lett.*, **32**, 163 (1975).
- (26) G. Lauer, W. Schäfer, and A. Schweig, *Chem. Phys. Lett.*, **33**, 312 (1975).
- (27) H.-L. Hase, G. Lauer, K.-W. Schulte, and A. Schweig, *Theor. Chim. Acta*, **48**, 47 (1978).
- (28) M. B. Robin, C. R. Brundle, N. A. Keubler, G. B. Ellison, and K. B. Wiberg, *J. Chem. Phys.*, **57**, 1758 (1972).
- (29) W. R. Harshbarger, N. A. Kuebler, and M. B. Robin, *J. Chem. Phys.*, **60**, 345 (1974).
- (30) H. Ogata, J. Kitayama, M. Koto, S. Kojima, Y. Nihui, and H. Kamada, *Bull. Chem. Soc. Jpn.*, **47**, 958 (1974).
- (31) W.-C. Tam, D. Yee, and C. E. Brion, *J. Electron Spectrosc. Relat. Phenom.*, **4**, 77 (1974).
- (32) J. A. Pople and D. L. Beveridge, "Approximate Molecular Orbital Theory", McGraw-Hill, New York, N.Y., 1970.
- (33) Y. Nakamo, S. Saito, and Y. Morino, *Bull. Chem. Soc. Jpn.*, **43**, 368 (1970).
- (34) H. W. Kroto, B. M. Landsberg, R. J. Suffolk, and A. Vodden, *Chem. Phys. Lett.*, **29**, 265 (1974).
- (35) T. Eicher and G. Frenzel, *Z. Naturforsch. B*, **20**, 274 (1965).
- (36) P. Vouros, *J. Heterocycl. Chem.*, **12**, 21 (1975).
- (37) The sum of inductive and conjugative influences of SO<sub>2</sub> on the  $\pi_{C=C}$  orbital of dimethylthiirene 1,1-dioxide amounts to  $-0.56$  eV.<sup>9</sup> This value is smaller than the corresponding sum of calculated influences of SO<sub>2</sub> on  $\pi_1$  of 2,3-diphenylthiirene 1,1-dioxide, which is  $-0.89$  eV (cf. Figure 5) because of the higher conjugative effect in the dimethyl derivative.
- (38) The calculated  $\pi$  charge transfer from PhC=CPh to M (using the CNDO/S procedure) is (in  $10^{-3}e$ ) for **6** 8.2, for **7** 245.4, for **8** 344.4, for **9** 82.2, and for **10** 81.4.
- (39) The CNDO/S conjugation energies (aromaticities) amount (in kcal/mol) to  $-4.55$  for **6**,  $-53.76$  for **7**,  $-52.84$  for **8**,  $-22.05$  for **9**, and  $-2.184$  for **10**.

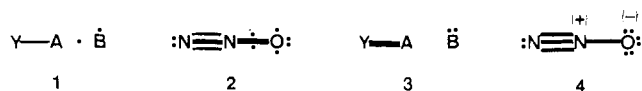
## "Increased Valence" When the Octet Rule Is Obeyed. A Reply to a Challenge

Richard D. Harcourt

Contribution from the Department of Physical Chemistry, University of Melbourne, Parkville, Victoria 3052, Australia. Received November 27, 1977

**Abstract:** Consideration is given to the use of the term "increased valence" when it is applied to the valence structure  $Y-A\cdot\dot{B}$  (I) relative to the standard valence-bond structure  $Y-A\dot{B}$  (II), each structure having a set of four electrons and three overlapping atomic orbitals ( $y$ ,  $a$ , and  $b$ ). One type of wave function for I is  $|y\bar{a}\psi_{abb}| + |\bar{y}a\psi_{abb}|$  with  $\psi_{ab} = a + kb$  and  $0 < k < \infty$ . From this wave function, it is deduced that a maximum of three electrons may simultaneously participate in bonding for I, and that for  $1 < k < \infty$ , the valence for A in I may exceed its value of unity in II. Therefore on at least two counts, I may be designated as an "increased-valence" structure relative to II. This point of view is contrasted with that expressed recently by Halgren et al. (ref 2).

The use of the term "increased valence"<sup>1</sup> when it is applied to the general valence structure **1** has recently been questioned.<sup>2</sup> This structure may be constructed<sup>1,3c-e</sup> whenever four electrons are distributed among three overlapping atomic orbitals centered on the three atoms Y, A, and B. For example, each set of four  $2p\pi$  and  $2p\pi'$  electrons of N<sub>2</sub>O has the electron distribution of **1** in the valence structure **2**. Although ten electrons seem somehow to be involved in bonding to the central nitrogen atom, an *apparent*<sup>3a-d</sup> rather than a real violation of the octet rule occurs in a minimal basis set description of **2**. Here I shall demonstrate that the designation of "increased valence" for valence structures **1** and **2** is appropriate in two senses, namely, (1) that more electrons participate in bonding for **1** and **2** than occur in the Lewis valence-bond structures **3** and **4** with electron-pair bonds, and (2) that the valence of the A atom in **1** and **2** can exceed that of unity and four for the same atom in **3** and **4**.



To demonstrate these propositions, we shall use Heitler-London rather than localized molecular orbital procedures to describe the YA bonding for **1** and **3**, thereby avoiding an effect that is associated<sup>4</sup> with electron spin and the overutilization

of the A-atom atomic orbital when localized molecular orbitals (or bond orbitals) are used to describe the YA and AB bonding electrons of **1**. From an examination of the Heitler-London type wave function for **1**, Halgren et al.<sup>2</sup> have attempted to demonstrate the converse of the second proposition.

For valence structures **3** and **1**, the  $S = 0$  wave functions are given by<sup>5,6</sup> eq 1 and 2, respectively, in which  $y$ ,  $a$ , and  $b$  are the overlapping atomic orbitals centered on the Y, A, and B atoms, and  $\psi_{ab} = (a + kb)/(1 + k^2)^{1/2}$  is the AB bonding molecular orbital that accommodates the electron of the AB bond of **1**. The Slater determinants of eq 1 and 2 generate the electron spin distributions ( $x \equiv s_z = +1/2$ ,  $o \equiv s_z = -1/2$ ) of **5** and **6** for

