

substituents in cyclopentadiene this MO is raised to 7.8 eV by hyperconjugative and inductive effects.⁹ For **5** and **6** we should expect similar values for the HOMO energies.¹⁰ However, the $\pi(a_2)$ MO of the cyclopentadienone derivatives **5** and **6** is stabilized by 0.7 and 0.8 eV, respectively, and has the same energy as the HOMO of unsubstituted cyclopentadiene and fulvene. This can be explained by assuming that opposite effects are operating on the HOMOs of **5** and **6** and compensating one another. As conjugative interactions with both the $\pi_{C=O}$ and the $\pi^*_{C=O}$ MOs are not allowed by symmetry, the observed stabilization can be only explained by the inductive influence of the C=O group.^{11,12}

These results clearly show that the above mentioned stabilization of the $\pi_{C=C}$ MO of **2** and **3** by 0.92 and 0.80 eV, respectively, relative to cyclopentene is mainly due to the inductive effect of the C=O group.

The high inductive effect of the carbonyl group is a consequence of the C⁺-O⁻ bond polarity which—and this is particularly noteworthy with regard to the antiaromaticity discussion^{4,13} of the [5]annulenones (**4–6**)—should be nearly constant in the whole series of compounds **1–6**.¹⁴ Suitable measures of the charge density on C₁ and O are the IPs of the n MOs (influenced by the charge on the O atom) and the chemical shifts of the C₁ atom in the ¹³C nmr spectra (influenced by the electron density on C₁). The IPs of the n MOs (measured values given above) and the δ (¹³C) values (**1**, 213.9;¹⁵ **2**, 208.1;¹⁵ 3-*tert*-butylcyclopent-2-enone, 207.0; **5**, 202.0; **6**, 201.5 ppm relative to the ¹³C resonance in tetramethylsilane) agree with the theoretical predictions.¹⁶

The results of this work suggest that the pe spectrum of the unsubstituted cyclopentadienone (**4**)¹⁷ should contain only one band (at about 9.3 eV) instead of two bands as in the spectra of **5** and **6**. They further show that the assumption that the HOMO energies of fulvene and cyclopentadienone (**4**) are equal^{13a} cannot be correct because of the inductive stabilization of this MO in **4**.

Acknowledgments. This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der

(9) R. Riemenschneider, *Z. Naturforsch. B*, **18**, 641 (1963). This work contains no indication of the positions of the two *tert*-butyl groups. According to the nmr spectrum it is 1,3-di-*tert*-butylcyclopentadiene.

(10) This expectation is based on the observation that the first IPs of 1,3- and 1,4-di-*tert*-butylbutadiene are the same: H. Bock and H. Seidl, *J. Amer. Chem. Soc.*, **90**, 5694 (1968), quoted by E. Heilbronner, V. Hornung, F. H. Pinkerton, and S. F. Thames, *Helv. Chim. Acta*, **55**, 289 (1972). Moreover, the expectation is directly supported by our observation that the $\pi(a_2)$ IPs of 1-phenyl-2,5-dimethylphosphole (8.0 eV) [W. Schäfer, A. Schweig, G. Märkl, H. Hauptmann, and F. Mathey, *Angew. Chem.*, **85**, 140 (1973); *Angew. Chem., Int. Ed. Engl.*, **12**, 145 (1973)] and 1-*tert*-butyl-3,4-dimethylphosphole (8.05 eV) [W. Schäfer, A. Schweig, and F. Mathey, unpublished results] are the same.

(11) Calculated (MINDO/2 method¹²) inductive stabilization of the $\pi(a_2)$ MO of cyclopentadienone relative to fulvene: 0.86 eV.

(12) M. J. S. Dewar, "The Molecular Orbital Theory of Organic Chemistry," McGraw-Hill, New York, N. Y., 1969.

(13) (a) E. W. Garbisch, Jr., and F. Sprecher, *J. Amer. Chem. Soc.*, **91**, 6785 (1969); (b) N. Trinajstić, *Rec. Chem. Progr.*, **32**, 85 (1971); (c) B. A. Hess, Jr., L. J. Schaadt, and C. W. Holyoke, Jr., *Tetrahedron*, **28**, 5299 (1972).

(14) Calculated (MINDO/2 method¹²) charges [10^{-2} e] on C₁ and O, respectively: **1**, 0.57 and -0.56; **2**, 0.57 and -0.57; **3**, 0.58 and -0.57; **4**, 0.60 and -0.54.

(15) G. C. Levy and G. L. Nelson, "Carbon-13 Nuclear Resonance for Organic Chemists," Wiley-Interscience, New York, N. Y., 1972.

(16) Calculated (MINDO/2 method¹²) IPs [eV] of the n MOs: **1**, 9.67; **2**, 9.53; **3**, 9.72; **4**, 9.71.

(17) For the synthesis of **4** cf. O. L. Chapman and C. L. McIntosh, *Chem. Commun.*, 770 (1971).

Chemischen Industrie. We thank Dr. I. L. Wilson for reading the manuscript.

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Received May 30, 1973

Through-Conjugation through the Sulfone Group in 2,5-Di-*tert*-butylthiophene 1,1-Dioxide¹

Sir:

In a preceding publication² we were able to detect by photoelectron spectroscopy weak through-conjugation³ and spiroconjugation^{4,5} in divinyl sulfone. Here we report results on 2,5-di-*tert*-butylthiophene 1,1-dioxide (**3**)^{3k} which show that in this compound there is an unexpected³ extraordinarily strong through-conjugation involving the sulfone moiety.

Figure 1 shows the photoelectron (pe) spectra of 2,5-di-*tert*-butylthiophene (**2**), **3**, and tetrahydrothiophene 1,1-dioxide (**4**). Figure 2 presents the correlation diagram of the highest occupied molecular orbitals (MOs) in 1,3-di-*tert*-butylcyclopentadiene (**1**),⁶ **2**, **3**, and **4**. We must assign, in agreement with CNDO/2⁷ calculations and in analogy with the MO sequence in other five-membered rings (cyclopentadiene,^{8a} furane,^{8b} pyrrole,^{8c} and thiophene^{8d}), the first two bands 1 and 2 in the pe spectrum of **3** to the antibonding combinations of the $\pi(1a_2)$ and the $\pi_2(\text{SO}_2)$ MOs [predominantly $\pi(1a_2)$] and the $\pi(2b_1)$ and $n_1(\text{SO}_2)$ MOs [(mostly $n_1(\text{SO}_2)$), respectively (cf. the representation of these MOs). Then follow, as the comparison with the pe spectrum of **4** indicates, several bands which must be assigned to the remaining three highest occupied MOs in the sulfone moiety.² Since these bands strongly

(1) Part 31 of "Theory and Application of Photoelectron Spectroscopy," part 30: H. Schmidt, A. Schweig, and G. Manuel, *J. Organometal. Chem.*, **55**, C1 (1973).

(2) C. Müller and A. Schweig, *Tetrahedron*, in press.

(3) See, *inter alia*: (a) G. Cilento, *Chem. Rev.*, **60**, 147 (1960); (b) C. C. Price and S. Oae, "Sulfur Bonding," Ronald Press, New York, N. Y., 1962; (c) G. Vincow, *J. Chem. Phys.*, **37**, 2484 (1962); (d) H. Mackle, D. V. McNally, and W. V. Steele, *Trans. Faraday Soc.*, **64**, 2060 (1968); (e) F. de Jong and M. Janssen, *J. Chem. Soc., Perkin Trans. 2*, 572 (1972); (f) G. G. Swain and E. C. Lupton, Jr., *J. Amer. Chem. Soc.*, **90**, 4328 (1968); (g) R. W. Taft, E. Price, I. R. Fox, I. C. Lewis, K. K. Anderson, and G. T. Davis, *ibid.*, **85**, 709 (1963); (h) L. A. Carpino and H. W. Chen, *ibid.*, **93**, 785 (1971); (i) L. A. Carpino, L. V. McAdams, III, R. H. Rynbrandt, and J. W. Spiewak, *ibid.*, **93**, 476 (1971); (j) W. L. Mock, *ibid.*, **89**, 1281 (1967); (k) W. L. Mock, *ibid.*, **92**, 7610 (1970).

(4) (a) H. E. Simmons and T. Fukunaga, *J. Amer. Chem. Soc.*, **89**, 5208 (1967); (b) R. Hoffmann, A. Imamura, and T. G. Zeiss, *ibid.*, **89**, 5215 (1967).

(5) (a) U. Weidner and A. Schweig, *Angew. Chem.*, **84**, 551 (1972); *Angew. Chem., Int. Ed. Engl.*, **11**, 537 (1972); (b) A. Schweig, U. Weidner, J. G. Berger, and W. Grahn, *Tetrahedron Lett.*, 557 (1973); (c) A. Schweig, U. Weidner, D. Hellwinkel, and W. Krapp, *Angew. Chem.*, **85**, 360 (1973); *Angew. Chem., Int. Ed. Engl.*, **12**, 310 (1973); (d) A. Schweig, U. Weidner, R. K. Hill, and D. A. Cullison, *J. Amer. Chem. Soc.*, **95**, 5426 (1973).

(6) W. Schäfer, A. Schweig, G. Maier, and T. Sayrac, *J. Amer. Chem. Soc.*, **96**, 279 (1974).

(7) J. A. Pople and D. L. Beveridge, "Approximate Molecular Orbital Theory," McGraw-Hill, New York, N. Y., 1970.

(8) (a) P. J. Derrick, L. Asbrink, O. Edquist, B. O. Jonsson, and E. Lindholm, *Int. J. Mass Spectrom. Ion Phys.*, **6**, 203 (1971); (b) *ibid.*, **6**, 161 (1971); (c) *ibid.*, **6**, 191 (1971); (d) *ibid.*, **6**, 177 (1971).

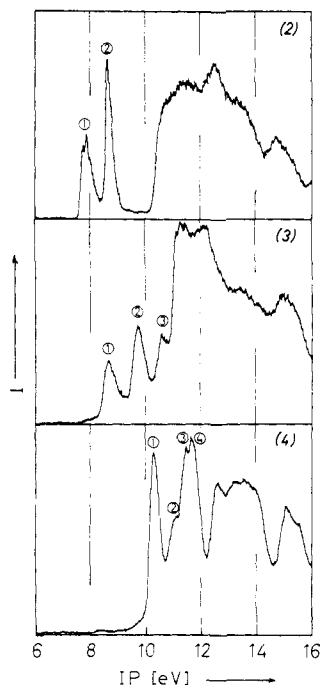


Figure 1. Photoelectron spectra of 2,5-di-*tert*-butylthiophene (2), 2,5-di-*tert*-butylthiophene 1,1-dioxide (3), and tetrahydrothiophene 1,1-dioxide (4). For the measured vertical ionization potentials and the assignment of bands, see Figure 2. The He-I (584 Å) photoelectron spectra have been recorded on a PS-18 spectrometer of Perkin-Elmer, Beaconsfield (England).

overlap with σ MOs due to the *tert*-butyl substituents,

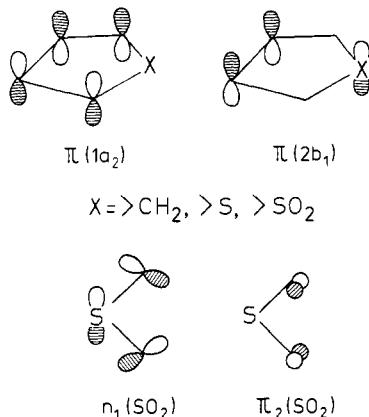


Figure 2. Correlation diagram of the highest occupied MOs of 1,3-di-*tert*-butylcyclopentadiene (1), 2,5-di-*tert*-butylthiophene (2), 2,5-di-*tert*-butylthiophene 1,1-dioxide (3), and tetrahydrothiophene 1,1-dioxide (4). The numbers shown above the levels are vertical ionization potentials (eV).

the sulfone moiety operates on the $\pi(1a_2)$ MO by an inductive effect of at least -0.85 eV.¹⁰

Again, the sulfone group may exert two effects on the $\pi(2b_1)$ MO, a stabilizing inductive and a destabilizing conjugative effect, and again, both effects cannot be separated for 3. However, from Figure 2 it follows— independently on an exact separation of both effects— that the $n_1(\text{SO}_2)$ MO is destabilized by 1.3 eV due to its interaction (hyperconjugation) with the suitably chosen “ $2b_1$ ” MO.¹² This result reveals that a strong through-conjugation (by hyperconjugation) involving the sulfone moiety exists in 2,5-di-*tert*-butylthiophene 1,1-dioxide.

Acknowledgments. This work was supported by the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, and the National Science Foundation. The helpful remarks of a referee are gratefully acknowledged.

(10) The inductive effect of the sulfone group on the π MO in 2,5-dihydrothiophene 1,1-dioxide is -1.3 eV.² The inductive effect exerted on the π_1 and π_2 MOs in 2,7-dihydrothiepin 1,1-dioxide is -1.36 and -1.22 eV, respectively.¹¹ The inductive plus conjugative effects measured for the π MO of methyl vinyl sulfone is -1.0 eV,² for the π_1 and π_2 MOs of 4,5-dihydrothiepin 1,1-dioxide -1.04 and -0.97 eV, and for the π_1 MOs of thiepin 1,1-dioxide -1.05 and -1.01 eV.¹¹ All results gathered so far suggest that the inductive effect of the sulfone moiety exerted on the aforementioned π MOs is about -1.2 eV and rather independent on the nature of the π MO itself. Furthermore, since the conjugative effects between the sulfone and π MOs in methyl vinyl sulfone, 4,5-dihydrothiepin 1,1-dioxide, and thiepin 1,1-dioxide seem not to exceed 0.2–0.3 eV, the spiroconjugative effect between the $\pi_2(\text{SO}_2)$ and $\pi(1a_2)$ MOs probably is also about 0.3 eV.

(11) C. Müller, A. Schweig, and W. L. Mock, submitted for publication.

(12) The hyperconjugative and inductive destabilization of the $\pi(2b_1)$ MO by the $>\text{CH}_2$ group is assumed to be the same in 1 as in cyclopentadiene. The latter destabilization was derived to be 1.0 eV: E. Heilbronner, R. Gleiter, H. Hopf, V. Hornung, and A. deMeijere, *Helv. Chim. Acta*, **54**, 783 (1971). If it is further assumed that the inductive stabilization of the $\pi(2b_1)$ MO amounts to -1.2 eV,¹⁰ we arrive at about 12.1 eV for the energy of the “ $\pi(2b_1)$ ” MO.

only band 3 is resolved in the spectrum of 3. This band corresponds to ionization from the $\pi_1(\text{SO}_2)$ MO (with two nodes, one node across each S–O bond). The bands 2–4 in the pe spectrum of 4 were previously² assigned to the antibonding lone pair combination $n_1(\text{SO}_2)$ ⁹ on the oxygen atoms, the bonding combination $n_2(\text{SO}_2)$,⁸ and the $\pi_2(\text{SO}_2)$ MO (with one node through the sulfur atom).

The sulfone moiety may exert two effects on the $\pi(1a_2)$ MO (with a node through the $>\text{SO}_2$ group): (i) a stabilizing inductive effect and (ii) a destabilizing spiroconjugative effect. Both effects cannot be separated for 3. However, since the $\pi(1a_2)$ MO in 3 is more stable by 0.85 eV than in 1, we must conclude that

(9) The $n_1(\text{SO}_2)$ and $n_2(\text{SO}_2)$ MOs, though localized mainly on the oxygen atoms, contain also significant contributions from the sulfur 3p AOs.

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Received May 30, 1973