

spectrum at low temperatures. The hydride region ^1H nmr spectrum is the X part of an A_2BX pattern and suggests that $\text{HNi}[\text{P}(\text{C}_2\text{H}_5)_3]_3^+$ at first undergoes a *mutual intramolecular exchange process* as the temperature is raised. (The two intense inner lines in the spectrum remain sharp as the rest of the spectrum broadens.) On further raising the temperature the spectrum collapses to a singlet due to intermolecular exchange. The associative nature of the latter process is revealed by the fact that addition of $\text{P}(\text{C}_2\text{H}_5)_3$ induces the collapse to a singlet at much lower temperatures. These line shape changes can again be rationalized in terms of eq 1, but now *the five-coordinate intermediate 2 must undergo intramolecular exchange more rapidly than it loses a ligand in a dissociative process*. These trends are in accord with our earlier observation that in d^8 HML_4 complexes the barriers to mutual exchange increase with increasing atomic number.⁷

Nmr line shape analyses are being carried out to obtain quantitative data for these systems. It is clear, however, from the qualitative data presented that this type of study can give insight into ligand exchange processes, rearrangements in transition states (or reaction intermediates), and the relative rates of cis-trans isomerization *vs.* intermolecular exchange to a degree not readily achieved by other approaches.

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(7) P. Meakin, E. L. Muetterties, and J. P. Jesson, *J. Amer. Chem. Soc.*, **94**, 5271 (1972).

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Inductive Effect of a Carbonyl Group. The Electronic Structure of [5]Annulenes¹

Sir:

In a recent publication² dealing with the photoelectron (pe) spectra of cyclopent-2-enone (2) and cyclopent-3-enone (3), a conjugative interaction between the $\pi_{\text{C}=\text{C}}$ MO and the vacant $\pi^*_{\text{C}=\text{O}}$ was postulated.³ As a consequence the $\pi_{\text{C}=\text{C}}$ MO is stabilized relative to cyclopentene. By means of the pe spectra of 2,5-di-*tert*-butylcyclopentadienone⁴ (5) and 3,4-di-*tert*-butyl-

(1) Part 27 of "Theory and Application of Photoelectron spectroscopy;" part 26: H. Schmidt and A. Schweig, *Tetrahedron Lett.*, 1437 (1973).

(2) D. Chadwick, D. C. Frost, and L. Weiler, *J. Amer. Chem. Soc.*, **93**, 4320 (1971).

(3) The theoretical reasoning throughout this work is based on the localized MO method. Considering the π MOs only two sorts of interaction between the ethylene (or *cis*-butadiene) and carbonyl moieties must be taken into account: (i) the inductive effect (field effect and polarization of the σ electrons) exerted by the charge polarized carbonyl group (due to its σ and π electrons) on the ethylene (or *cis*-butadiene) π MOs and (ii) the conjugative interaction between all occupied and vacant π MOs (as modified by effect i) of both systems.

(4) G. Maier and F. Bosslet, *Tetrahedron Lett.*, 1025 (1972).

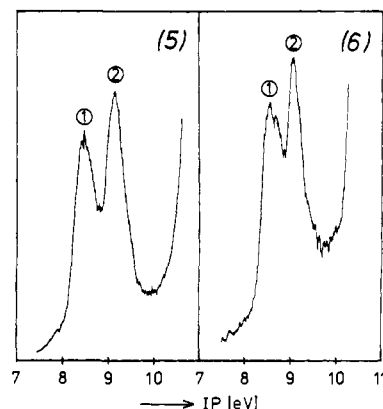


Figure 1. Sections of the photoelectron spectra of 2,5-di-*tert*-butylcyclopentadienone (5) and 3,4-di-*tert*-butylcyclopentadienone (6). The measured vertical ionization potentials [eV] are: for (5) 1, 8.50; 2, 9.15; for (6) 1, 8.60; 2, 9.10. The He-I (584 Å) photoelectron spectra were recorded on a PS-18 spectrometer from Perkin-Elmer, Beaconsfield (England).

cyclopentadienone⁵ (6), we are now able to explain the observed stabilization of the π MO by the inductive effect of the $\text{C}=\text{O}$ group.³

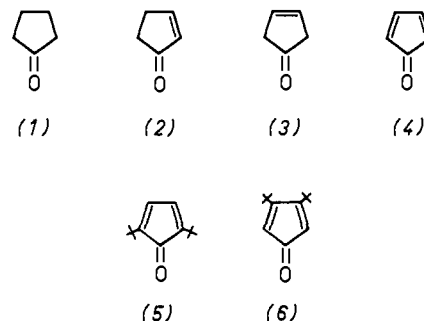
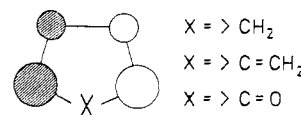


Figure 1 shows sections of the pe spectra of 5 and 6. Both spectra exhibit two bands at nearly the same position below the σ continuum. Band 2 (5, 9.15 eV; 6, 9.10 eV) must be assigned to ionization from the oxygen lone pair,⁶ the corresponding lone pair ionizations (IPs) of 1, 2, and 3 are, for comparison, (1) 9.25 eV,² (2) 9.34 eV,² and (3) 9.44 eV.² Band 1 (5, 8.50 eV; 6, 8.60 eV) then is due to ionization from the π (a_2) MO (node along the $\text{C}=\text{O}$ bond; *cf.* the representation of this MO).



The $\pi(a_2)$ HOMOs ("highest occupied MOs") of cyclopentadiene (8.57 eV⁷) and fulvene (8.55 eV⁸) have the same symmetry and topology as the HOMO in cyclopentadienone (4). On introducing two *tert*-butyl

(5) G. Maier, G. Fritschi, and R. Hoppe, *Angew. Chem.*, **82**, 551 (1970); *Angew. Chem., Int. Ed. Engl.*, **9**, 529 (1970).

(6) The determination of MO energies throughout this work is based on the validity of Koopmans' theorem: T. Koopmans, *Physica (Utrecht)*, **1**, 104 (1934).

(7) P. J. Derrick, L. Asbrink, O. Edquist, B. O. Jonsson, and E. Lindholm, *Int. J. Mass. Spectrom. Ion Phys.*, **6**, 203 (1971).

(8) E. Heilbronner, R. Gleiter, H. Hopf, V. Hornung, and A. de Meijere, *Helv. Chim. Acta*, **54**, 783 (1971).

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. Schaad, 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).

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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.

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(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).