Tetrahedron Letters No. 16, pp 1471 - 1474, 1974. Pergamon Press. Printed in Great Britain.

SPLITTING OF THE DEGENERATE ACETYLENIC π MOS; A PROBE FOR RING STRAIN [1]

Hartmut Schmidt and Armin Schweig [+]
Fachbereich Physikalische Chemie der Universität
D-3550 Marburg/Lahn, Biegenstrasse 12, Germany

Adolf Krebs
Institut für Organische Chemie der Universität
D-6900 Heidelberg, Im Neuenheimer Feld 7, Germany

(Received in UK 26 February 1974; accepted for publication 7 March 1974)

As Figure 1 shows, the splitting between the π MOs of acetylene depends strongly on the angle α , i.e. the deviation from the colinear arrangement of the C-H bonds and the triple bond. The destabilization of the π_y MO is mainly due to the negative overlap ($S_{1.205\ \AA} = -0.29$) between the $2p_x$ AOs contributing to this MO for $\alpha \neq 0$ ($0 < \alpha \leq 90^{\circ}$). Recently synthesized systems, namely cyclooctyne (1)[2], 3,3,8,8-tetramethylcyclooctyne (2)[3], 3,3,7,7-tetramethylcycloheptyne (3)[4], and 3,3,6,6-tetramethyl-1-thiacycloheptyne (4)[5] allow an experimental examination of these theoretical predictions.

Figure 2 shows the photoelectron (pe) spectra of 3 and 4 and Figure 3 displays the experimental[6] correlation diagram for the highest

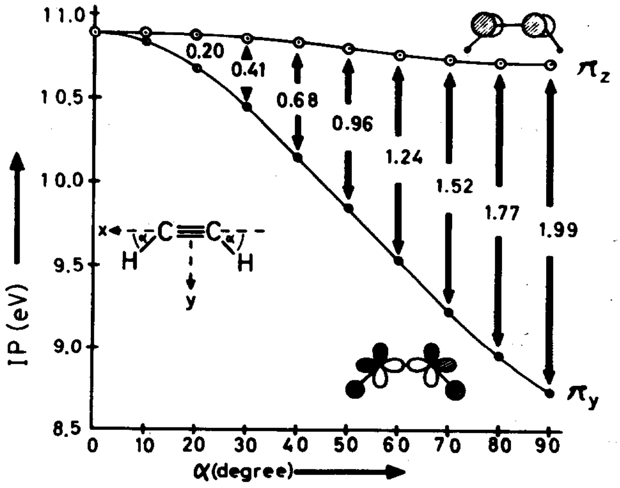


Figure 1

Calculated (MINDO/2 method[12]) splitting of the π_y and π_z MOs in acetylene versus the angle α .

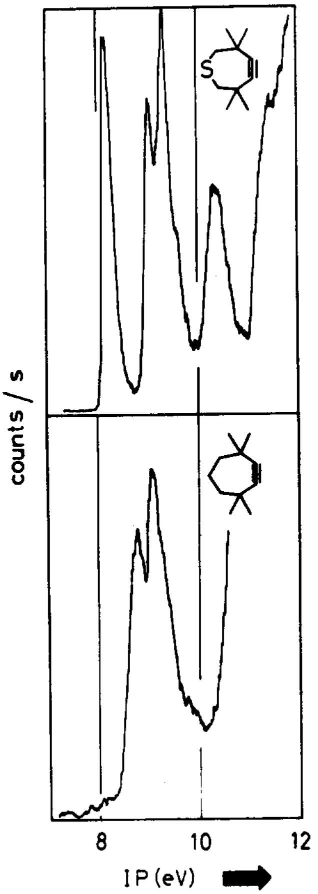


Figure 2

Photoelectron spectra [13] of molecules 3 and 4.

occupied MOs (the π_y and π_zMOs of the triple bond and the n_π lone pair MO on the sulphur atom of 1 to 4 and of 3,3,6,6-tetramethyl-1-thiacycloheptane(5). As the spectra and correlation diagram (Figure 3) reveal, the degenerate acetylenic πMOs are not split in either 1 or 2 . For 1, α is 21.5° [7] . The expected splitting (Figure 1) is only about 0.2 eV and thus not resolved in the pe spectrum of 1 [8]. In the case of 3, α amounts to 34.2° [9]. In agreement with the predicted splitting of about 0.5 eV, the corresponding bands in the pe spectra (Figure 2) of 3 and 4 are split (measured splitting = 0.32 eV for 3 and 0.31 eV for 4). These results show that with increasing α , i.e. increasing ring strain, the splitting of the degenerate acetylenic πMOs grows and can be observed, for the first time, with the cycloheptyne systems.

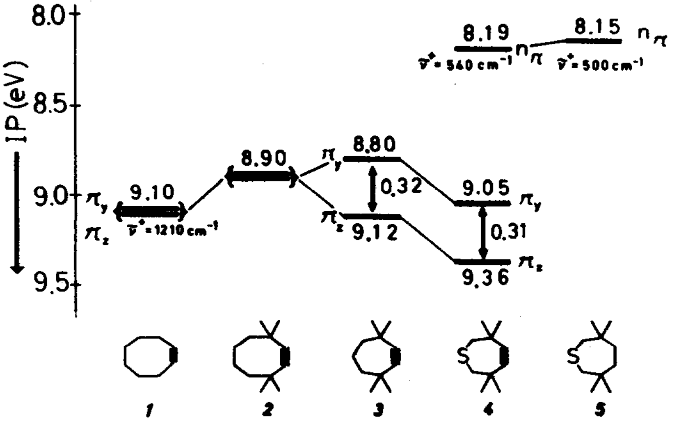


Figure 3

Correlation diagram for the highest occupied MOs of molecules 1 to 5.

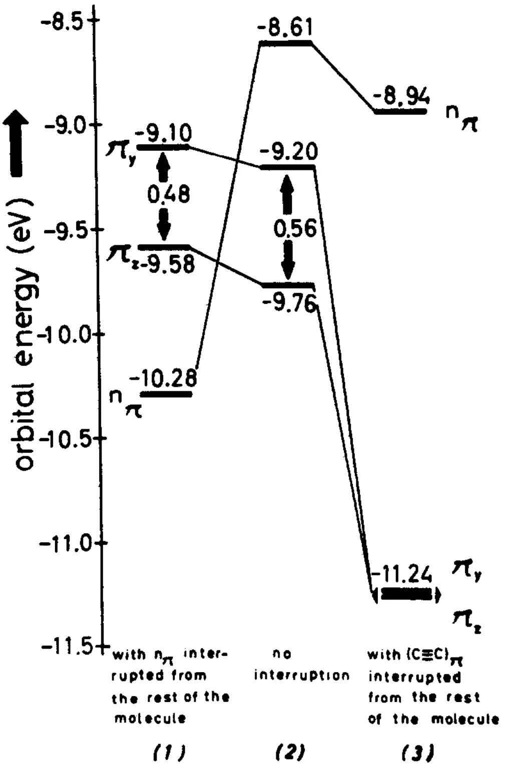
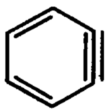


Figure 4

CNDO/S [11] calculations on 4 at three stages [(1) to (3)] of conjugative interruption.

From our results we may additionally expect that for cyclohexyne systems (e.g. the benzyne system 6) the splitting of the acetylenic π MOs should be as high as about 1 eV. Moreover, our findings suggest that the increase in the π_y MO energy in strained cycloalkynes is the source of the enhanced reactivity of the triple bond in these systems.

In order to confirm that the observed splitting in 4 is due to ring strain and not to possible transannular interaction between the n_{π} and the π_y MOs we used a method [10] which permits one to interrupt the conjugation of a selected portion of molecule with the rest of the system in conjunction with an extended CNDO/S method [11]. The results are shown in Figure 4. Obviously, the splitting in case (2) is only insignificantly higher than in case (1), indicating that the transannular n_{π} / π_y interaction plays no rôle.



6

References

1. Part 46 of "Theory and Application of Photoelectron Spectroscopy". This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie. - Part 45: W.Schäfer, A.Schweig, G.Maier, T.Sayrac, and J.K.Crandall, submitted for publication.
2. A.T.Blomquist and L.H.Liu, J.Amer.Chem.Soc. 75, 2153 (1953); G.Wittig and H.L.Dorsch, Liebigs Ann.Chem. 711, 46 (1968).
3. A.Krebs, unpublished results.
4. A.Krebs and H.Kimling, Angew.Chem. 83, 540 (1971).
5. A.Krebs and H.Kimling, Tetrahedron Lett. 761 (1970).
6. Based on the validity of Koopmans' theorem: T.Koopmans, Physica 1, 104(1934).
7. J. Haase and A.Krebs, Z.Naturforsch. 26a, 1190 (1971).
8. C.Batich, O.Ermer, E.Heilbronner, and J.R.Wiseman, Angew.Chem. 85,302(1973).
9. J.Haase and A.Krebs, Z.Naturforsch. 27a, 624 (1972).
10. C.Müller and A.Schweig, Angew.Chem., in press.
11. K.W.Schulte and A.Schweig, Theoret.chim.Acta, in press.
12. M.J.S.Dewar, The Molecular Orbital Theory of Organic Chemistry, McGraw-Hill, New York 1969.
13. The He-I (584 Å) photoelectron spectra were recorded on a PS-18 spectrometer from Perkin-Elmer, Beaconsfield (England).