

Cyclic Acetylenic Compounds

Thomas J. Sworski

Citation: [The Journal of Chemical Physics](#) **16**, 550 (1948); doi: 10.1063/1.1746936

View online: <http://dx.doi.org/10.1063/1.1746936>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/16/5?ver=pdfcov>

Published by the [AIP Publishing](#)

Articles you may be interested in

[Molecular modelling of openchain and cyclic oxathia compounds and relations to liquidliquid extraction results](#)

AIP Conf. Proc. **330**, 418 (1995); 10.1063/1.47803

[Erratum: Electron attachment to cyclic anhydrides and related compounds](#)

J. Chem. Phys. **63**, 598 (1975); 10.1063/1.431893

[Electron attachment to cyclic anhydrides and related compounds](#)

J. Chem. Phys. **59**, 3550 (1973); 10.1063/1.1680519

[Ultrasonic Investigation of Molecular Properties of Liquids, Cyclic Compounds](#)

J. Acoust. Soc. Am. **20**, 585 (1948); 10.1121/1.1916957

[Raman Spectra of Acetylenic Bromides, Iodides, and Ketones and of Some Cyclic Compounds](#)

J. Chem. Phys. **12**, 156 (1944); 10.1063/1.1723928



of adsorption hysteresis, almost certainly too sweeping. In the first place, adsorption hysteresis is known to be greatly aggravated in some cases by the presence of air⁸—an impurity almost inevitably present during measurements of the contact angle. In the second place, adsorption hysteresis occasionally persists even when scrupulous attention has been paid to removal of impurities;⁹ it is also known in films on water.¹⁰ Finally, it is now widely recognized that phase transformations can occur in films on solids;¹¹ and by analogy with phase changes in bulk matter and also from general considerations, it is only to be expected that such transformations would sometimes occur excessively slowly. Indeed, these delayed phase changes may well be the cause of adsorption hysteresis itself, in many cases;¹² but in any event it is to be expected that the time lag would often be so long that the phase change would not be completed within the time of an experiment.

No doubt the hysteresis of adsorption and, therefore, of the contact angle may, *in principle*, be completely eliminated in all cases where impurities are absent by allowing sufficient time to elapse before taking the measurements of θ ; but, judging from common experience with the adsorption of vapors, the time required would occasionally be impracticably long. Consequently, *under conditions attainable in practice*, it seems that in a residue of cases, at least, hysteresis of the contact angle will persist despite the most careful precautions.

- ¹ W. D. Harkins and R. Dahlstrom, *Ind. Eng. Chem.*, **22**, 897 (1930).
- ² D. H. Bangham and R. I. Razouk, *Trans. Faraday Soc.*, **33**, 1459 (1937).
- ³ D. H. Bangham, *Trans. Faraday Soc.*, **33**, 805 (1937).
- ⁴ D. H. Bangham, *J. Chem. Phys.*, **14**, 352 (1946).
- ⁵ J. B. M. Herbert, *Trans. Faraday Soc.*, **26**, 118 (1930). D. H. Bangham and S. Mosallam, *Proc. Roy. Soc.*, **166A**, 559 (1938). F. Durau, *Ann. d. Physik*, **87**, 365 (1928). F. C. Tompkins, *Trans. Faraday Soc.*, **32**, 643 (1936). J. Holmes and P. H. Emmett, *J. Phys. Chem.*, **51**, 1262 (1947). R. T. Davis, T. W. de Witt, and P. H. Emmett, *J. Phys. Chem.*, **51**, 1232 (1947).
- ⁶ W. D. Harkins and F. M. Fowkes, *J. Am. Chem. Soc.*, **62**, 3380 (1940).
- ⁷ W. D. Harkins, *Advances in Colloid Chemistry* (edited by J. Alexander, 1946), Vol. VI, p. 61.
- ⁸ J. W. McBain, "Sorption of gases and vapours by solids." S. Brunauer, "The physical adsorption of gases and vapours."
- ⁹ B. Lambert and A. G. Foster, *Proc. Roy. Soc.*, **136A**, 375 (1932).
- ¹⁰ N. K. Adam, *Physics and Chemistry of Surfaces*, p. 56.
- ¹¹ D. H. Bangham, N. Fakhoury, and A. F. Mohamed, *Proc. Roy. Soc.*, **138A**, 162 (1932); **147A**, 152 (1934). S. J. Gregg, *J. Chem. Soc.*, 696 (1942). W. D. Harkins and G. Jura, *J. Chem. Phys.*, **12**, 112, 114 (1944); *J. Am. Chem. Soc.*, **66**, 1356 (1944); **68**, 1941 (1946).
- ¹² S. J. Gregg, *J. Chem. Soc.*, 706 (1942); *Trans. Faraday Soc.*, to be published.

Cyclic Acetylenic Compounds

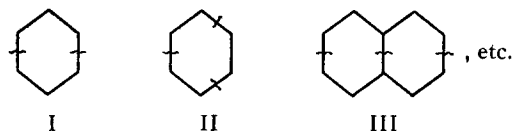
THOMAS J. SWORSKI*

University of Notre Dame, Notre Dame, Indiana
March 24, 1948

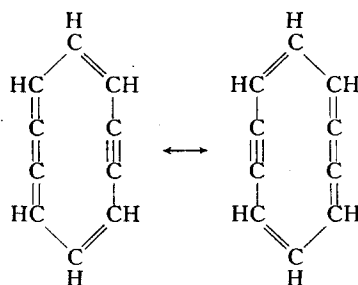
CYCLIC conjugated ring systems have been of experimental and theoretical interest in recent years. For example, the work of Prosen, Johnson, and Rossini¹ indicates quite definitely that cyclooctatetraene lacks the stability inherent in the benzene ring. This has been explained on the basis of a non-planar structure which, although permitting maximum overlapping of the σ -orbitals, does not permit maximum overlapping of the π -orbitals.

It is of interest to consider whether the quantum mechanical representation of hybridized carbon atoms may permit the prediction of stable, planar, conjugated ring

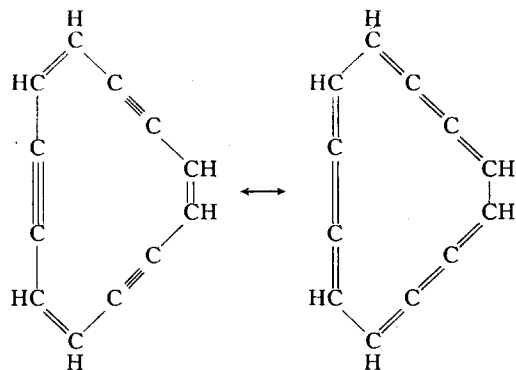
structures of more than six carbon atoms. It is the purpose here to present a few illustrative examples of such a potential series. These can be shown to be derived from the corresponding benzene derivatives by the insertion of either the linear acetylenic group ($-\text{C}\equiv\text{C}-$) or the linear cumylene group ($=\text{C}=\text{C}=$) at appropriate places as follows.



Operation I leads to the following resonating structure.



Operation II similarly produces the following interesting resonating structure.



Examination of the bond angles of these compounds readily verifies their planar and strainless nature. It is further evident that each carbon atom will have a p -orbital which may be perpendicular to the ring and thus capable of overlapping the adjacent orbitals on either side to form a continuous molecular π -orbital just as for benzene. In addition, the acetylenic carbons are presumed to have localized π -orbitals in the plane of the ring. The prediction of resonance in these structures implies conjugative properties for the triple bond similar to those for the double bond.

It is of interest to establish experimentally the validity of such a prediction. Synthetic work on the preparation of ring systems of these types is under way in these laboratories through dimerization of phenylpropionyl chloride and by condensation of glyoxal with acetylene diGrignard.

* Work by the writer at the University of Notre Dame is assisted by the Office of Naval Research of the United States Navy Department under contract N6 ori 165, T.O.II.

¹ Prosen, Johnson, and Rossini, *J. Am. Chem. Soc.*, **69**, 2068 (1947).