

Hysteresis of the Contact Angle

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specific results for C₈D₈ which appear to confirm the D₄ structure. If C₈H₈ and C₈D₈ have this structure, these molecules have a species of vibration A2 (see Herzberg, "Infrared and Raman Spectra," D. Van Nostrand Company, New York, 1945, p. 252), which is infra-red active and Raman inactive. There are four vibrations of this species in both C₈H₈ and C₈D₈. We have located unequivocally three strong bands, presumably of this species, at 670, 800, and 3004 cm⁻¹ in C₈H₈ and at 527, 720, and 2236 in C₈D₈. The location of a fourth vibration will be discussed when this work is published in detail. Here we wish only to make the point that prolonged exposure of the Raman spectrum has failed to reveal any sign of the 670 and 800 frequencies in C₈H₈ or of 527 and 720 in C₈D₈, although these over-exposed spectra have produced a total of some forty Raman overtones in C₈H₈.

In the symmetry D_{2d}, which has been suggested on the basis of x-ray and electron diffraction studies,7 all infra-redactive species are Raman-active also. The spectroscopic data accordingly appear to favor strongly the D4 over the D_{2d} structure.

One of the striking features of the Raman spectra of both C₈H₈ and C₈D₈ is the collection of four strong lines of low frequency. These are presumably to be assigned to ringpuckering vibrations analogous to the non-planar benzene ring vibrations. There should be four such frequencies in both the D₄ and D_{2d} structures. In the D_{2d} structure, however, one of the four is forbidden in both Raman and infrared spectra, whereas four are Raman-active in D4. While the assignment of these four lines to the puckering vibrations is not an absolute necessity, the large gap of more than 250 cm⁻¹ between the highest of these and the next lowest Raman line in both C₈H₈ and C₈D₈ is convincing support for such assignment and for the D₄ structure.

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¹ Lippincott and Lord, J. Am. Chem. Soc. 68, 1868 (1946).
² Cf. Cope and Overberger, J. Am. Chem. Soc. 69, 976 (1947).
² Flett, Cave, Vago, and Thompson, Nature 159, 739 (1947).
⁴ Bastiansen, Hassel, and Langseth, Nature 160, 128 (1947).
⁴ The D₄ structure, which has been called the "crown structure" by some, consists of a puckered eight-membered ring with alternate single and double bonds. The puckering occurs in such a way that a fourfold axis (C4) is present, so that the ring has a saw-toothed appearance when viewed edgewise. Even-numbered carbon atoms lie in the same plane, which is parallel to the plane in which the odd-numbered carbon atoms lie. An analogous statement holds for the hydrogen atoms. By symmetry all carbon atoms are equivalent as are all hydrogen atoms. It should be noted that the D₄ structure implies optical isomerism.
⁵ R. C. Lord, Jr., Proceedings of the Colloquium on Molecular Structure, Paris, May 27, 1947 (to be published in J. de Chim. physique).
⁵ Lippincott and Lord, Symposium on Molecular Spectra, Ohio State University, June 1947.
' Kaufman, Fankuchen, and Mark, Nature 161, 165 (1947); J. Chem. Phys. 15, 414 (1947), Personal communication from Professor V. Schomaker.

Hysteresis of the Contact Angle

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HE angle of contact θ of a liquid against a solid is profoundly influenced by the presence of an adsorbed film on the unimmersed portion of the solid (and formed by spreading from the liquid, or by adsorption from the vapor phase, or both). This is implicit in Harkins and Dahlstrom's treatment of the subject in 1930, but was first explicitly and quantitatively discussed by Bangham and Razouk² in 1937; they arrived at the expression

$$F_L - F_V = \gamma_L \cos \theta, \tag{1}$$

where F_L and F_V are the diminutions in free energy when 1 cm² of the clean solid (i.e., free from film) is immersed in the liquid and exposed to the vapor, respectively; γ_L is the free surface energy of the liquid. In effect, almost all other workers had taken $F_L = \gamma_L \cos \theta$.

For a mobile film, Bangham³ has shown that F_V may be equated with π , the surface pressure of the film; consequently, Eq. (1) may be written

$$F_L - \pi = \gamma_L \cos \theta. \tag{2}$$

This form of the Bangham-Razouk relationship possesses the merit of expressing the dependence of θ on the adsorbed film in terms of a simple property of the latter, its surface pressure; and this is calculable, in principle^{3,4} and often in practice, from the adsorption isotherm of the vapor on the solid by means of the integrated Gibbs adsorption equation: $\pi = RT \int_0^p \Gamma d \ln p$ (Γ moles = adsorption per unit area of the solid and p=pressure of the vapor). In particular it suggests an immediate connection between hysteresis of the contact angle and hysteresis in adsorption;4 in this latter phenomenon the pressure P (and with it the surface pressure π) is greater on the "adsorption-increasing" run than on the "adsorption-decreasing" one, for a given adsorption Γ. It should be noted that hysteresis can occur with nonporous adsorbents⁵ and is not confined to porous bodies, as is often supposed.

Now in measurements of the advancing contact angle, θ_a , the adsorbed film (surface pressure = π_a) is in the process of formation by spreading or by adsorption from the vapor phase; it corresponds to the "adsorption-increasing" run of a vapor adsorption experiment. But in measurements of the receding angle, θ_r , the film $(\pi = \pi_r)$ adjacent to the line of contact has recently been covered with the bulk liquid, and it corresponds to the "adsorption-decreasing" run. If adsorption hysteresis occurs, $\pi_a > \pi_r$, consequently $\theta_a > \theta_r$, i.e., there is hysteresis of the contact angle.

To eliminate any difference between θ_a and θ_r it is necessary that $\pi_a = \pi_r$, and this requires (i) that adsorption hysteresis be eliminated, and (ii) that the pressure p over the film shall be the same during both measurements. To achieve (ii) is difficult in practice unless ϕ be chosen as ϕ_0 . the saturated vapor pressure. Attainment of (i) calls for a number of precautions, notably that ample time be allowed for attainment of adsorption equilibrium, and that impurities be absent. Both these points are implicitly, though not explicitly, taken into account in the procedure adopted by Harkins and Fowkes,6 whereby they have been able to eliminate hysteresis of the contact angle in a large number of cases.

Nevertheless, Harkins' assertion7 that the "advancing and receding angles obtained by nearly all investigators other than those in this laboratory is due to improper preparation of the surface and poor techniques in making the measurements," is, in view of the known characteristics 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.

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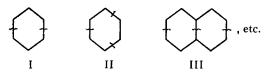
Cyclic Acetylenic Compounds

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YCLIC 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 $(-C \equiv C -)$ or the linear cumulene group (=C=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

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 phenylpropiopyl chloride and by condensation of glyoxal with acetylene diGrignard.

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