Tetrahedron Letters No. 46, pp 4623 - 4628, 1973. Pergamon Press. Printed in Great Britain.

FLEXIBLE AROMATIC RINGS

Hans Wynberg*

Department of Organic Chemistry,

and

W.C. Nieuwpoort and H.T. Jonkman,

Department of Theoretical Chemistry,

The University, Groningen, Holland.

(Received in UK 14 September 1973; accepted for publication 8 October 1973)

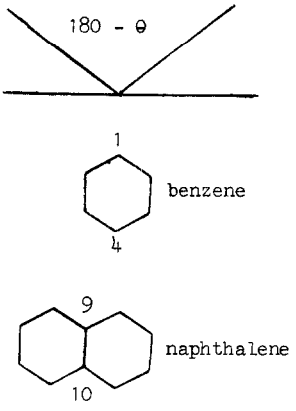
It has been an article of faith among organic chemists that simple and condensed aromatic molecules are flat and rigid frameworks upon which reactions occur.[1] On the basis of accumulating experimental evidence as well as ab initio calculations we wish to criticize this dogma. We suggest that mono- and polynuclear aromatic hydrocarbons are flexible molecules capable of 5°- 20° deviations from a plane in the ground state.[2]

Consider the experimental evidence: (a) [2,2]-Paracyclophane (I)[3] has severely bent benzene rings as proven[9] by Brown 20 years ago. Neither this deformation, nor the strain energy of 31 kcal/mole[10] prevents the molecule from undergoing normal aromatic substitution reactions.[11] (b) Benzo(c)phenanthrene (II), one of many overcrowded[12], non-resolvable aromatic hydrocarbons, is non-planar in the solid state as shown by the X-ray data of Schmidt.[13] (c) A number of optically active helicenes (e.g. III) can be racemized with relative ease.[14] The X-ray data on two helicenes clearly show the non-planar, helical structure.[15] A racemization mechanism based on in- and out-of-plane stretching and bending of the aromatic rings is proposed. (d) Corannulene (IV) has been synthesized and its structure determined by X-ray analysis.[16] This bowl-shaped molecule (IV) consists of five non-planar benzene rings. A corannulene monocarboxylic acid (IVa, R=COOH) is chiral if "umbrella-like" inversion of the bowl does not occur. The resolution has been attempted but has not yet been successful.[17] The inversion of IV need not proceed via a planar transition state. The latter is energetically the most demanding one. Experiments

Table I

Out of plane deformation energies (kcal/mol) for benzene and naphthalene.

θ	$\Delta E^{1)}$	$\Delta E^{2)}$
0°	0	0
1°	0.029	-
2°	0.109	0.097
5°	0.671	0.609
10°	2.693	2.460
15°	6.092	-
20°	10.908	9.969



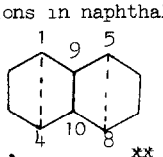
1) benzene, 1-4 bending

2) naphthalene, 9-10 bending

Table II

Simultaneous deformations in naphthalene

Total angle*	bending along atoms		ΔE kcal/mole
5	1-4		0.632
5	9-10		0.509
10	1-4; 9-10		1.330
10	1-4; 9-10		1.155
10	1-4; 5-8		1.177
10	1-4; 5-8		1.353
15	1-4; 9-10; 5-8		1.962
15	1-4; 9-10; 5-8		1.615



* Total angle = /180-9/. Absolute value

** The drawings show highly exaggerated bending of course. The actual 5° would look like this

with models (e.g. an umbrella) clearly show that inversion can occur via an undulating motion starting at any point along the perimeter. Resolution and racemization of corannulene would greatly add to our understanding of the flexible benzene model.

(e) Properly constructed circulenes[18] (e.g. V) are chiral, if a sufficiently rigid non-planar ground state exists. Our failure to date[14] to resolve such a circulene again suggests greater aromatic ring flexibility than normally visualized.

Theoretical evidence: In order to obtain some theoretical data on the out of plane deformability of aromatic rings a number of simple all electron ab initio SCF-MO calculations were carried out on benzene and naphthalene. The computations were performed with the program GAUSSIAN 70[19] employing the standard 1STO/3G basis set of Gaussian orbitals for C and H.[20] In the calculations on benzene the molecule was bent along the 1 - 4 axis and the energy was computed as a function of the bending angle (Table I). For naphthalene two sets of calculations were carried out. In the first set (Table I), similar to benzene, the molecule was bent along the 9 - 10 bond. The second set was directed to an investigation of the additivity of deformation energies by calculating the effect of simultaneous deformations of 5° along two or more axes. The results are shown in Table II. In all calculations the H atoms were taken to move rigidly with the C atoms to which they are bound and the C-H and C-C bond lengths were kept constant (R_{CH}=1.10 Å; R_{CC}=1.39 Å). The numbers listed cannot be taken too literally because of the inherent limitations of the present calculations. These limitations are:

i) The use of a minimal set of expansion functions which prevent us from approaching the Hartree-Fock limit.

ii) the impossibility of the nuclear framework to relax to the energetically most favorable structure associated with each deformation angle.

iii) the unknown behaviour of the electron correlation energy as a function of the deformation angle.

The first two limitations can be partly or wholly removed depending on the amount of computer time one is willing to use. A calculations of the correlation error, however, is beyond our present capabilities. Nevertheless, for small deformations up to 5°, possibly 10°, we believe that our results represent useful estimates for the energies involved. This belief is based on the generally satisfactory results which are obtained for hydrocarbon structures with the type of calculation employed here[21] and the fact that our calculation on benzene yields a bending force constant of 0.628 mdyne/Å which compares well with one of the two independent sets of force constants that

have been derived from the out of plane vibrational frequencies of benzene.[22] Table II shows a fair degree of additivity with an average energy of about 0.6 kcal/mol per deformation of 5°.

Discussion:

The out-of-plane deformation of an aromatic molecule is a well established spectroscopic property. This fact has -in our opinion- not been brought to bear properly on problems in organic chemistry. The proper consequence of this fact is -aromatic rings are flexible. Our thinking in organic chemistry should reflect this fact.

(a) The benzene to "Dewar" benzene photochemical transformation, although well described in terms of orbital and spin-state events[23] has never had an adequate geometrical description. How- in fact- and when does the "planar" benzene molecule become the book-like Dewar benzene, Franck - Condon principle notwithstanding? Our viewpoint is that either in the ground state or excited state bent-benzene modes may well be the precursors to Dewar benzenes. The reverse argument, namely the formation of a bent-benzene ring via a Dewar-like intermediate has recently been invoked by Jones Jr.[24] in describing the synthesis of a [7]paracyclophane.

(b) Westheimer's classical calculations[25] on the racemization of optically active biphenyls did not include ring bending modes.[25] The process may well become better understood if a flexible benzene viewpoint is included.

(c) The synthesis of [2,2]paracyclophane, [8]paracyclophane and similar aromatic compounds where the product incorporates a bent-benzene ring as proven by X-ray analysis[2,3] is, by itself, evidence that such bent structures occur at some point along the reaction coordinate.

(d) It seems reasonable to assume that substituents on the aromatic ring increase the latters tendency to deform. It is noteworthy that 1,2,4-tri-t-butylbenzene was one of the first molecules to undergo a light induced transformation to a Dewar benzene.[23]

(e) A 5 - 20° bending mode of one benzene ring must lead to a highly flexible situation for a poly nuclear aromatic hydrocarbon. The concept -non-rigid, flexible aromatics- may thus widen our synthetic and mechanistic viewpoint. The synthesis of novel cyclophanes, containing for example polynuclear aromatic hydrocarbons, may well be easier than imagined hitherto.

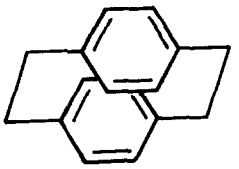
(f) The "flexible benzene" viewpoint is naturally applicable to non-benzenoid aromatic systems. A priori it may be argued that small aromatic rings (cyclopropylium cation, thiophene) should be more rigid whereas large aromatic rings([13] annulene, porphyrins) should be more flexible than benzene. Obviously additional factors, such as the nature of the heteroatom, the charge on the

ring and non-bonded interactions will complicate this simple picture.

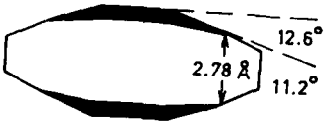
(g) It seems to us that arguments against the bent-benzene viewpoint based on destabilization through reduced π orbital overlap are invalid. To a first approximation the loss of overlap on one side of the ring is compensated by increased overlap on the orther side (see drawing V).

References.

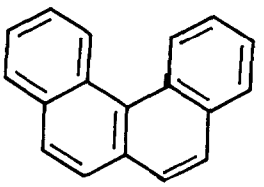
1. Cf. "Organic Chemistry" by N.L. Allinger, H.P. Cava, D.C. de Jongh, N.A. Le Bel and C.L. Stevens, Worth Publ., Inc., N.Y., 1971, p. 229 and the many textbooks with virtually identical drawings of the benzene ring.
2. A number of authors have previously drawn attention to some aspects of the "bent" nature of the benzene ring. Noteworthy is the "Bent- and Battered Benzene ring" review article by Donald Cram and his wife.[3] Garratt[4] observes: "The planar, symmetrical hexagon structure for benzene is the equilibrium configuration," and "...benzene can be more easily distorted by out-of-plane vibrations than by in-plane vibrations." E.M. Arnett[5] carefully summarizes the case for a warped benzene ring in o-di-t-butylbenzenes citing H. Dauben[6], J. Dale[7], and N.L. Allinger concluding: "...the argument(s) are not conclusive". The X-ray analysis[8] of o-di-t-butylaromatics, showing planar or nearly planar aromatic rings seems to have ended the controversy concerning the 'bent' nature of crowded monocyclic aromatics.
3. D.J. Cram and J.M. Cram, Account Chem.Res., 4, 204 (1971).
4. "Aromaticity" by P. Garratte, McGraw-Hill, 1971, p. 33.
5. E.M. Arnett, J.C. Sanda, J.M. Bollinger and M. Barber, J.Amer.Chem.Soc., 89, 5389 (1967).
6. H.J. Dauben Jr., J.D. Wilson and J.L. Laity, ibid., 91, 1991 (1968).
7. J. Dale, Chem.Ber., 94, 2821 (1961).
8. G.J. Visser, A. Vos, Ae de Groot and H. Wynberg, J.Amer.Chem.Soc., 90, 3253 (1968); A. van Bruijnsvoort, L. Eilermann, H. van der Meer and C.H. Stam, Tetrahedron Lett. 2527 (1968).
9. J. Brown, J.Chem.Soc., (1953); See K.N. Trueblood, J. Bernstein and H. Hope for a refined structure analysis as cited in ref. 2.
10. R.H. Boyd, Tetrahedron Lett. 22, 119 (1966).
11. D.J. Cram, W.J. Wechter and R.W. Kierstead, J.Amer.Chem.Soc., 80, 3126 (1958).
12. M.S. Newman, in "Steric Effects in Organic Chemistry", ed. M.S. Newman, J. Wiley and Sons, N.Y., 1956, p. 475.
13. F.H. Herbstein and G.M.J. Schmidt, J.Chem.Soc., 3302 (1954); K. Lonsdale, H.J. Milledge and K.V. Krishna Rao, Proc. Roy. Soc. A 255, 82 (1960).
14. M.S. Newman and D. Lednicer, J.Amer.Chem.Soc., 78, 4765 (1956). H. Wynberg and M.B. Groen, Chem.Commun., 964 (1969); R.H. Martin and H.J. Marchant. Activation enthalphies vary from 25 - 42 kcal/mole.
15. M.B. Groen, G. Stulen, G.J. Visser and H. Wynberg, J.Amer.Chem.Soc., 92, 7218 (1970). D.A. Lightner, D.T. Hefelfinger, G.W. Frank, T.W. Powers and K.N. Trueblood, Nature, Phys.Sc., 232, 124 (1971).
16. W.E. Barth and R.G. Lawton, J.Amer.Chem.Soc., 93, 1730 (1971).
17. Personal Communication Prof. Lawton, May 1973.
18. J.H. Dopper and H. Wynberg, Tetrahedron Lett. 763 (1972); unpublished exp. J.H. Dopper.
19. A CDC 6600 version of this program was made available to us by Drs. W.J. Hehre and D. Kracht.
20. R. Ditchfield, W.J. Hehre and J.A. Pople, J.Chem.Phys., 52, 5001 (1970).
21. W.J. Hehre, R. Ditchfield, L. Radom and J.A. Pople, J.Amer.Chem.Soc., 92, 4796 (1970).
22. F.A. Miller and B.L. Crawford Jr., J.Chem.Phys., 14, 282 (1946).
23. E.E. van Tamelen, Accounts Chem.Res. 5, 186 (1972).
24. A.D. Wolff, V.V. Kane, R.H. Levin and M. Jones Jr., J.Amer.Chem.Soc., 95, 1680 (1973).
25. F.H. Westheimer's in "Steric Effects in Organic Chemistry", ed. M.S. Newman, J. Wiley and Sons, N.Y., 1956, p. 523 , Westheimer states (p. 550): "but the (benzene) rings themselves are so stiff that they are only slightly deformed"- offering no evidence for the assumption.



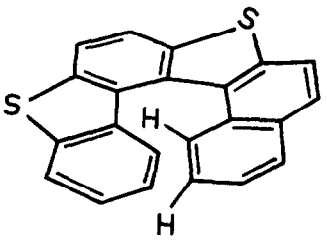
I



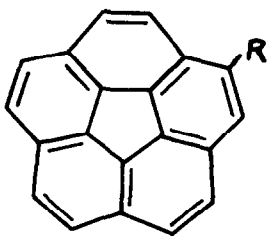
I



II



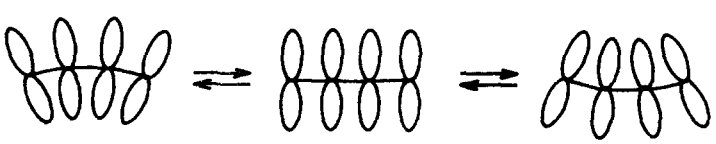
III



IV

IV

V



VI