Bent Benzene—Boat or Chair?

George G. Hall
Shell Centre for Mathematical Education, University of Nottingham, Nottingham, UK NG7 2RD

It is argued that a benzene ring should bend into boat form when compressed inside a molecule.

Embedded benzene rings are component parts of many organic molecules. Even when the conjugation inside the ring is little affected, the surrounding structure may constrain the ring and distort it. In this paper it is pointed out that the distortion to boat form is the one requiring least energy and so is the form most likely to be found. The combination of forces required to achieve various distortions is discussed.

Results and Discussion

When the carbon atoms of benzene are moved from their flat hexagonal configuration elastic forces act to oppose the distorting forces. Stretching, bending and torsion forces, involving two, three and four atoms at a time, may all contribute. The geometry of the distorted molecule will depend on the magnitude and direction of the applied forces exerted by the surrounding structure. Alternatively, the new atomic positions will be those for which the additional potential energy due to these forces and to the distortion is least. To the question 'What distortion of the benzene ring requires the least potential energy?' there is a simple answer. The distortion with the lowest potential energy is the boat form. It is this low energy which ensures that, when the molecule vibrates, its normal mode of vibration with the lowest frequency is the boat mode. In normal modes the frequency is determined by both the elastic forces and the effective mass. The low energy out-of-plane modes, however, have very similar effective masses so that their frequencies parallel the elastic forces.

The lowest normal mode of benzene is ν_{20} (in the notation of Herzberg).[1] This is an E_{2u} mode and one form of the degenerate vibration is the boat form. In it the H atoms move in phase with the C atoms. The A_{2u} mode has the next lowest frequency but it has the H atoms wagging out of the plane of the undistorted ring and so is not relevant to this argument. The third lowest mode is ν_8, which is B_{2g}, and has the chair form. These three modes are out of the molecular plane. The lowest planar mode is ν_{18}, which is E_{2g} and represents a compression of the ring, either at two *para* C atoms or along two opposite sides, depending on phase.

The observed spectra and a force constant calculation enable frequencies to be assigned to these three modes despite the fact that the first is very weak and the second is forbidden. The experimental results[2] are shown in Table 1.

Table 1 Low frequency modes of benzene

Mode	Symmetry	Form	Frequency/ cm^{-1}	Symmetry force constant
ν_{20}	E_{2u}	boat	398	0.1617
ν_8	B_{2g}	chair	707	0.1928
ν_{18}	E_{2g}	planar	606	0.633

From the force constant analysis the energy needed to distort the benzene ring itself can be calculated. The symmetry force constants (in aJ units) found by Pulay *et al.*[3] are shown in the final column of Table 1. The two columns show the same ordering of the boat and chair modes. The relative magnitude of the boat and chair forms is understandable when it is realised that the boat form can be achieved, approximately, by bending the molecule along a line through two *para* C atoms (four adjacent C atoms lie on each of two planes) whereas the chair form requires two such bendings (the C atoms lie on three planes). The ease of ring distortions out of the plane compared with those in it can be understood when it is remembered that the first depend on the torsion forces, which are relatively weak, and the second on the valence angle bending forces, which are stronger. Although the planar mode has a low frequency this is due partly to its higher effective mass. As the final column shows, its force constant is considerably larger than for the out-of-plane modes so the resistance to planar distortion of the ring will be large.

The distortion found in a molecule must also depend on the forces applied to the ring through its substituents. If only one C atom is affected then the ring will not be distorted since it can adapt by adjusting its position or orientation. Similarly, if two atoms in *ortho* positions are affected then, provided that the CC bond length is unchanged, the angles in the ring will be unchanged and it will remain flat. If two *meta* atoms are compressed then the ring will bend into boat form to accommodate the strain. Compression at two *para* positions can produce either a planar or a non-planar boat distortion and, in general, the result will be a mixture with the non-planar dominating since it is so much easier. On the other hand, tension at two *para* positions will produce a distortion in which the planar component dominates since it alone permits the *para* atoms to move further apart. To obtain a chair form at least three C atoms (all *meta*) need to be compressed.

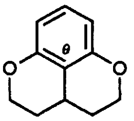

Fig. 1 Benzene ring compressed by a saturated environment

Confirmation of the presence of boat forms has been obtained in two publications. Begley *et al.*[4] report the structure of formylcitran and acetylcitran, which each have one embedded benzene ring, and demonstrate the presence of a very similar boat distortion in both molecules. Again, Begley *et al.*[5] report on the structure of bruceol and one of its derivatives.

The relevant common feature of these molecules is the three ring system shown in Fig. 1.

One ring is benzene and the other two are non-planar saturated rings containing oxygen atoms and having various substituents. These two connect with the benzene at three adjacent C atoms. The presence of compression is shown by the fact that θ, the angle inside the ring at the central C, is 118°. This atom and the C atom *para* to it lie above the plane of the remaining four C atoms. The benzene ring system shows the same boat distortion. In all these molecules the ring is held at three consecutive C atoms and buckles along a line through the centre atom. The other surrounding substituent groups are irrelevant to the distortion.

Acknowledgements

The author thanks his colleague Prof. L. Crombie who stimulated his interest in this phenomenon and provided references.

References

1 G. Herzberg, *Infra-red and Raman Spectra*, Van Nostrand, New York, 1945.

2 S. Brodersen and A. Langseth, *K. Dan. Vidensk. Selsk. Mat. Fys. Skr. 1*, 1956, 1.

3 P. Pulay, G. Fogarsi and J. E. Boggs, *J. Chem. Phys.*, 1981, **74**, 3999.

4 M. J. Begley, L. Crombie, R. W. King, D. A. Slack and D. A. Whiting, *J. Chem. Soc., Perkin Trans. 1*, 1977, 2393.

5 M. J. Begley, L. Crombie, D. A. Slack and D. A. Whiting, *J. Chem. Soc., Perkin Trans. 1*, 1977, 2402.

Paper 3/00620D
Received 1*st February* 1993
Accepted 14*th April* 1993