Tetrahedron Letters Vol. 21, pp 1757 - 1760
©Pergamon Press Ltd. 1980. Printed in Great Britain

0040-4039/80/0429-1757$02.00/0

HOW STRAINED IS THE "FLAT" BENZENE RING IN SUPERPHANE ?

Hiizu Iwamura* and Morimatsu Katoh
Institute for Molecular Science, Myodaiji, Okazaki 444, Japan

Hiroshi Kihara
Faculty of Domestic Science, Hagi Women's Junior College,
Maeobata, Hagi 758, Japan

Summary: The strain energy in the bowl-shaped benzene ring incorporated in superphane has been estimated by the MO theoretical calculations at 20.6 kcal/mole (the 4-31 G calculations). The π-orbitals on the ring are not parallel to each other, but loss in the π-resonance energy does not appear to be serious. The strain in the σ-framework is considered to be responsible for most of the destabilization.

The elucidation of the chemical bonding in deformed benzene rings is indispensable for a thorough understanding of chemistry of cyclophanes and other bridged aromatic compounds.[1] Recently a new type of the strained ring was introduced by an epoch-making synthesis of superphane by Boekelheide and coworkers.[2] As opposed to the boat, chair and skew forms usually found in cyclophanes, a pair of the benzene rings in superphane are characterized by their deformation to a bowl shape. Whereas the six-carbon skeleton in the benzene ring is flat, the six side-chain carbons attached to the ring are out of the plane, although they make another plane of their own parallel to and separated by 0.526 Å from the first one.[3]
Our naive questions are: i) How much is this bowl-shaped benzene ring strained ? and ii) What do the π-orbitals in the ring look like ?

We have carried out the semi-empirical and the ab initio SCF MO calculations for the ground states of the C_6H_6 molecule fixed in a geometry simulating the experimental structure of superphane determined by the X-ray crystallography,[3] the latter structure being in good agreement with the one

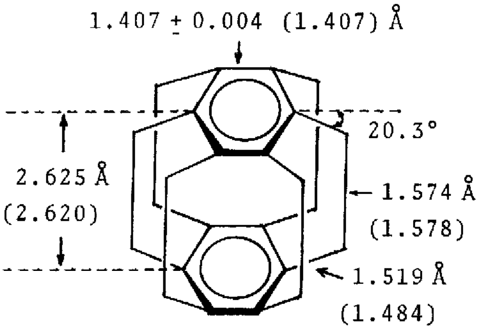

Figure 1. The X-ray[3] (and π-SCF-force-field theoretical[4]) structures of superphane.

obtained theoretically by Lindner using the molecular mechanics (see Figure 1).[4]

In Table 1 are given the heats of formation and the dissected energy terms of the bowl-shaped benzene rings in a various degree of the out-of-plane deformation. In reference to the heat of formation of the regular benzene molecule with D_{6h} symmetry, the benzene ring of superphane is found to be strained by 20.3 (MNDO), 15.5 (MINDO/3), and 20.6 (*ab initio*; the 4-31 G basis) kcal/mole. The values are slightly larger than those (6 ~ 10 kcal/mole) of the boat benzene in a number of cyclophanes,[1] and are comparable to those (17 ~ 20 kcal/mole) in [2.2]paracyclophadiene [5] and of the skew benzene ring found in the middle ring of triply-layered paracyclophanes.[6] The theoretical strain energy value of 17.8 kcal/mole is obtained for the skew ring by our present 4-31 G calculations. Assuming that the total strain energy in superphane as being 79 kcal/mole,[4] we may conclude that strain would be roughly equally distributed between the two benzene rings (2 × 20 kcal/mole) and the side chains plus interring interaction if any.

Table 1. Heats of formation (kcal/mole) and the MINDO/3 dissected energy terms (eV) for the bowl-shaped benzene rings.

	ΔH_f		$\Delta\Delta H_f$		
α[a]	MNDO	MINDO/3[b]	MNDO	MINDO/3	4-31 G
0	21.2	28.4	0	0	0
15	32.6	37.2	11.4	8.7	——
20	41.5	43.9	20.3	15.5	20.6
25	53.0	52.6	31.8	24.2	——

	one center [7]		neighboring two center [7]		
				$E_{C_1C_2}$	
α	ΣE_C	ΣE_H	ΣE_N	total	resonance
0	-607.72	-56.02	-193.01	-20.20	-21.51
20	-608.01	-56.02	-192.05	-20.09	-21.39
25	-608.18	-56.01	-191.51	-20.03	-21.32

a) angle of the out-of-plane displacement of the hydrogen atom.

b) the bond lengths optimized at fixed α.

Turning now to the shape of the π-orbitals on the ring, we show the contour representation of the π-electron density in superphane as given in Figure 2. The originally planar trigonal ring carbons are now slightly pyramidal in superphane. As a result, the π-orbitals are not perpendicular to the ring plane but are deflected by ca. 10°. One may intuitively conclude that π-bonding will be disfavored outside of the bowl and could be favored inside the cage as compared to the bonding in the normal benzene ring. The effect can be visualized by the electron density distribution map of the π-bond as in Figure 3. Two additional cross-sections of the π-orbitals with planes parallel to and displaced by 0.5 Å above and below the ring plane are given in Figure 4.

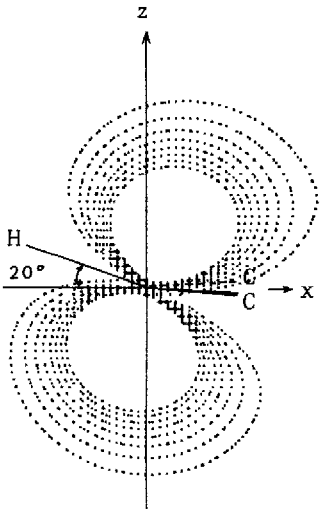

Figure 2. π-Electron distribution in the mirror plane passing through the ring carbon of the bowl-shaped benzene.

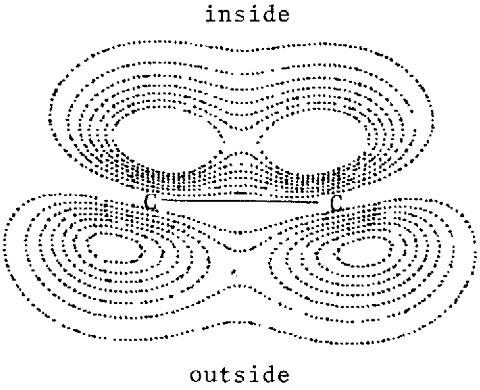

Figure 3. The contour representati of the π-bond on the bowl-shaped benzene ring. Contours at 0.168, 0.144, 0.120,... and 0.024 e $Å^{-3}$.

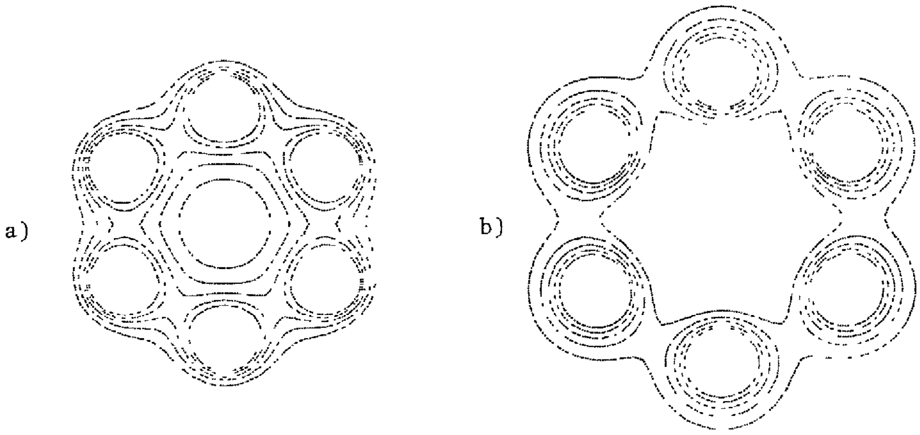

Figure 4. Illustration of the dense and diffuse π-bonds inside and outside of the bowl, respectively. Contours at 0.264, 0.216, 0.168, 0.120 and 0.072 e $Å^{-3}$ in the planes parallel to and displaced by 0.5 Å a) above (inside) and b) below (outside) the ring plane.

The energy partitioning studies reveal that the resonance term due to the neighboring two center C_1-C_2 moiety increases by 0.12 eV on going from $\alpha = 0°$ to 20° and appears to be responsible for the destabilization of the bowl-shaped benzene ring (see Table 1). It is further shown by the analysis of the MO correlation diagram that the energies of molecular orbitals #17, 20 and 21 having the p_z character, namely, the orbitals corresponding to the ones with a_{1u} and e_{1g} symmetry (the latter doubly degenerated) in the planar benzene molecule, are not affected materially by deformation to a bowl shape. Thus the increased and decreased π-bondings inside and outside of the bowl, respectively, are considered to cancel each other. Contrary to our initial expectation, it is degenerated orbitals #18 and 19 rich in p_x and p_z character, respectively, that are destabilized meaningly. It is therefore concluded that the destabilization of the bowl-shaped benzene ring should be due not to the slight loss of alignment in the π-orbitals on the ring but to the strain in the σ-framework made of p_x and p_y orbitals.

Lastly we point out that nothing unusual can be found in the π-bonding of the benzene ring in superphane as compared to that of the planar benzene molecule except that symmetry of the π-orbitals with respect to the ring plane is lost in the former. There would be no handicap to the formation of π-complexes in superphane. Thus the apparent inertness of superphane against electrophilic reagents[3] should be attributed to the difficulty in rehybridization of the ring carbon to form σ-complexes.

References

1) H. Iwamura, H. Kihara, S. Misumi, Y. Sakata, and T. Umemoto, Tetrahedron Lett., 615 (1976); Tetrahedron, **34**, 3427 (1978).

2) Y. Sekine, M. Brown, and V. Boekelheide, J. Am. Chem. Soc., **101**, 3126 (1979).

3) V. Boekelheide, private communication and the paper presented at the 12th Symposium on Structural Organic Chemistry, Matsumoto, Sept. 29th, 1979.

4) H. J. Lindner, Tetrahedron, **32**, 753 (1976).

5) C. L. Coulter and K. N. Trueblood, Acta Cryst., **16**, 667 (1963); P. K. Ganzel and K. N. Trueblood, Acata Cryst., **18**, 958 (1965).

6) K. Nishiyama, M. Sakiyama, S. Seki, H. Horita, T. Otsubo, and S. Misumi, Tetrahedron Lett., 3739 (1977).

7) M. S. Gordon, J. Am. Chem. Soc., **91**, 3122 (1969); H. Fischer and H. Kollmar, Theoret. Chim. Acta, **16**, 163 (1970); H. Iwamura, H. Kihara, K. Morio, and T. L. Kunii, Bull. Chem. Soc. Jpn., **46**, 3248 (1973).

(Received in Japan 4 February 1980)