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Communications

The Origin of the Symmetrical Structure of Benzene. Is the σ or the π Frame Responsible? An ab Initio Study of the Effect of HCC Bond Angle Distortion

Summary: Ab initio molecular orbital calculations have been carried out to determine the effect of symmetrical HCC bond angle distortions on both the π and σ frames of benzene.

Sir: There is some debate in the literature about the origin of the symmetrical structure of benzene. Applying an avoided-crossing model, Shaik et al.[1,2] proposed that the main symmetrizing forces in this molecule originate from the σ frame, the π frame being more stable when localized, e.g., preferring a cyclohexatriene frame. Ab initio calculations support this conclusion,[3] but the issue has been controversial.[4-7]

This study was prompted by the observation of pronounced (if not complete) bond fixation of the central ring in angular [3]phenylene[8a] and tris(benzocyclobutadieno)benzene.[8b] While the accepted rationale for this effect has been one based on aromaticity grounds (one of the resonance structures of the ring in question being strongly destabilized because of its benzocyclobutadienoid nature), it was of interest to establish to what extent the bond angle distortion induced by strained ring fusion was influential in this regard. Hence, quantitative molecular orbital calculations were performed scrutinizing the effect of applying a Mills–Nixon[9] type deformation to benzene, by simultaneous symmetrical bending of neighboring CH bonds as shown in Figure 1. For comparison, similar calculations were executed for ethene and 1,3-butadiene.

The reported data were obtained by employing the GAUSSIAN 82[10] series of programs. All molecules were fully optimized by using the 3-21G[11] basis set. The "90° benzene", **3c**, was also optimized at HF/6-31G*[12] and MP2/3-21G[13] levels of theory in order to examine the effect of polarization functions and configuration interactions, respectively, on the geometry. The MNDO[14] method yielded similar results.[15] In contrast to other investigations,[2-5] no assumption was made with respect to CC bond lengths.

Table I. Optimal 3-21G Geometries and Energies for 1–3

compd	θ, deg	R^1, Å	R^2, Å	total energy, Hartrees	relative energy, kcal mol^{-1}
1a	121.9	1.315		−77.60099	0.0
1b	110.0	1.326		−77.59159	5.9
1c	100.0	1.349		−77.56570	22.1
1d	90.0	1.397		−77.51654	53.0
2a	121.2 (HC_1C_2) 118.7 (HC_2C_1)	1.320	1.479	−154.05394	0.0
2b	110.0	1.331	1.476	−154.03961	9.0
2c	100.0	1.335	1.439	−153.99113	39.4
2d	90.0	1.404	1.423	−153.84608	99.1
3a	120.0	1.385	1.385	−229.41945	0.0
3b	100.0	1.459	1.346	−229.31867	63.2
3c	90.0	1.562	1.319	−229.18708	145.8

Table II. Frontier Molecular Orbital Energies of 1–3[a]

compd		HOMO		HOMO-1		HOMO-2
1a	[π][b]	−0.3798 (0.0)	[σ][b]	−0.4990 (0.0)		
1b		−0.3774 (1.5)		−0.5035 (−2.9)		
1c		−0.3741 (3.6)		−0.5572 (−36.5)		
1d		−0.3671 (7.9)		−0.4928 (3.9)		
2a	[π][b]	−0.3254 (0.0)	[π][b]	−0.4444 (0.0)	[σ][b]	−0.4894 (0.0)
2b		−0.3230 (1.5)		−0.4437 (0.4)		−0.4928 (−2.1)
2c		−0.3199 (3.5)		−0.4420 (1.5)		−0.4914 (−1.2)
2d		−0.3128 (7.9)		−0.4373 (4.4)		−0.4832 (3.9)
3a	[π][b]	−0.3390 (0.0)	[σ][b]	−0.4914 (0.0)	[π][b]	−0.5025 (0.0)
3b		−0.3424 (−2.1)		−0.4649 (16.6)		−0.5046 (2.4)
3c		−0.3498 (−6.8)		−0.4276 (40.1)		−0.4940 (9.1)

[a] Orbital energies in Hartrees. Relative energies (kcal mol^{-1}) in parentheses. [b] Orbital type.

Table III. Optimized HF/6-31G* and MP2/3-21G Geometries and Energies of 3c

	R^1, Å	R^2, Å	E, Hartrees
HF/6-31G*	1.529	1.329	−230.47374
MP2/3-21G	1.579	1.346	−229.73734

Applying the bond-angle distortions shown in Figure 1 to **1** and **2** results in the expected Mills–Nixon-type behavior. Thus, as the HCC angles deviate from the optimum values,[10] the CC bonds connecting the distorted hydrogens (R^1) lengthen and in **2** C_2C_3 (R^2) shortens (Table I). The orbital changes (Table II) are in accord with the Walsh postulate.[16] Thus, the π energies (the HOMO in ethene and the HOMO and HOMO-1 in 1,3-butadiene) increase with the total energies, and in **1** the p_π coefficients remain constant (in **2** there is a slight change in order to minimize the antibonding interactions between C_2 and C_3). The highest σ orbitals (HOMO-1 in **1** and HOMO-2 in **2**) are stabilized initially (because of smaller antibonding

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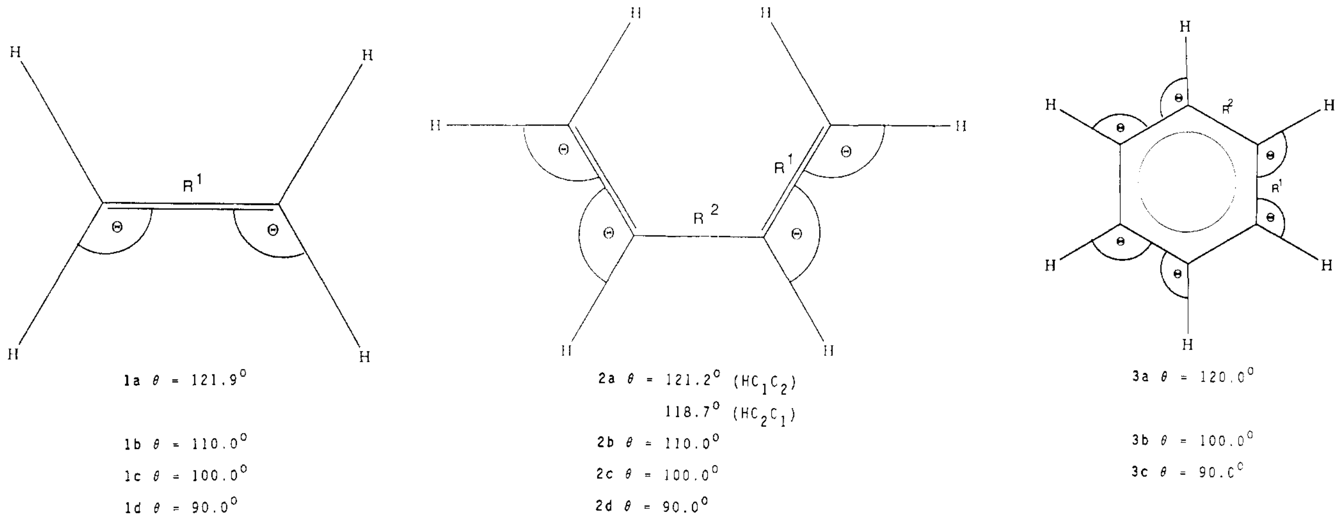

Figure 1. Bond angles used in the calculations of 1-3.

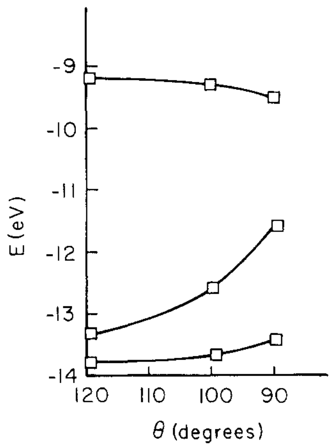

Figure 2. The changes in the energies of the HOMO (top curve), HOMO-1 (center curve), and HOMO-2 (bottom curve) in **3a-c**.

interactions and mixing of the C_{2s} orbital due to rehybridization) but destabilized for larger deviations from the optimal θ value.

How does the same distortion affect benzene? The geometry and energy change in a fashion that is analogous to that observed for **1** and **2** (Table I). Thus, as θ deviates from 120°, R^1 lengthens, R^2 shortens, and the total energy is raised substantially. The molecular orbitals, however, behave very differently when compared to those in **1** and **2** (Table II, Figure 2). The doubly degenerate HOMO's (which are of π type) lower in energy when going from **3a** to **3b** and **3c**, by 2.1 and 6.8 kcal mol^{-1}, respectively. The other occupied π orbital (HOMO-2) is destabilized by about the same respective amount (2.4 and 9.1 kcal mol^{-1}, see Table II). Therefore, although the total energy is raised by 145.8 kcal mol^{-1} along the series, *the π energy is lowered by 4.5 kcal mol^{-1}*. On the other hand, HOMO-1, a doubly degenerate σ orbital is substantially destabilized (16.6 and 40.1 kcal mol^{-1}, respectively) during this procedure, acting as if it were the HOMO according to Walsh's postulate.[17]

The structure of **3c** was optimized also at the HF/6-31G* and MP2/3-21G levels of theory. The results (Table III) indicate that the observed bond alternation is not an artefact of an inflexible basis set or insufficient correlation interaction.

In summary, our results are in agreement with Shaik's understanding of the system, which regards a symmetrical π structure as being imposed by the σ frame. In addition, the much discussed Mills-Nixon effect[18] is confirmed by these calculations, implying that the bond fixation present in the central ring of the angular phenylenes must originate, at least partly, from the bond-angle distortion imposed by the attached four-membered rings.

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[17] At the suggestion of a referee, similar calculations were carried out (MNDO) on benzene, freezing the CC bonds lengths. As might be expected, the relevant orbital changes corresponding to those in Table II are much smaller, HOMO and HOMO-2 staying practically invariant, HOMO-1 increasing in energy by increments that are about half of those in Table II.

[18] See: Hiberty, P. C.; Ohanessian, G.; Delbecq, F. *J. Am. Chem. Soc.* 1985, *107*, 3095 and references therein.

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Accelerating Effect of a Remote Cationic Center on the Cope Rearrangement. Evidence of σ-Participation by a Norbornane C-C Bond in a Novel Tetracyclic Framework[†]

Summary: The first observation of acceleration of [3,3]-sigmatropic (Cope) rearrangement, by a remote cationic center, in a novel tetracyclic framework embodying a norbornyl moiety, is described.

[†] Dedicated with respect and affection to Prof. M. V. George on his 60th birthday.