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ab initio CALCULATION OF BOAT BENZENES IN BIS(2,4,6-TRI-t-BUTYLPHENYL)PHOSPHINIC CHLORIDE

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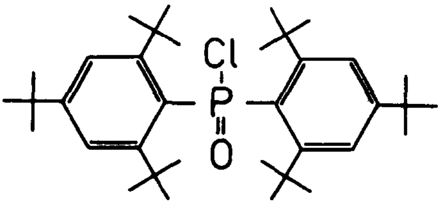
SUMMARY: ab initio Calculation of the benzene skeletons of the titled compound indicated that the molecule suffers 61.4 kcal/mol higher energy than that of flat benzene rings and that the boat benzene form is even more stable than the envelope or chair form benzene.

We have recently reported formation[1] and X-ray crystallographic analysis[2] of a very crowded molecule, bis(2,4,6-tri-t-butylphenyl)phosphinic chloride (1) which carries two very bulky 2,4,6-tri-t-butylphenyl groups attached geminally on one phosphorus atom. Its reactivity is remarkably degenerated because of the steric congestion around the phosphorus atom compared with phosphinic chlorides in general.[3] The X-ray analysis indicated deformation of the two benzene rings to a boat shape due to the strong intramolecular repulsion.



(1)

Figure 1 indicates the mean side profile of the benzene ring of half of the molecule (1), where hydrogens and ortho t-butyl groups are omitted for clarity.

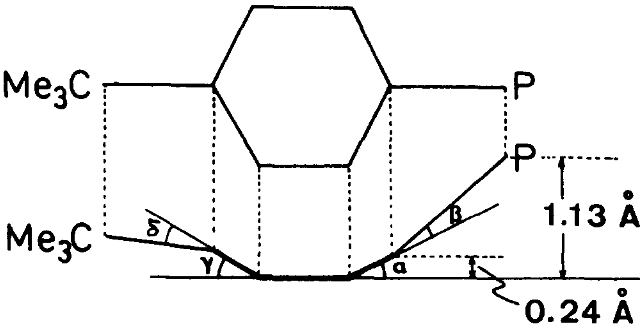


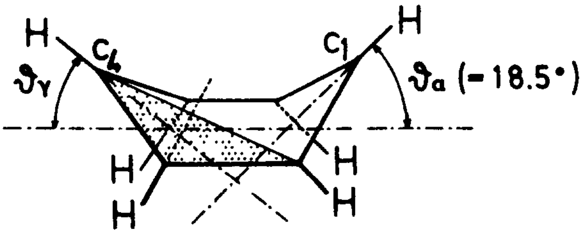
Fig.1

$\alpha = 18.5°$ $\beta = 10.0°$ $\gamma = 10.3°$ $\delta = 3.7°$

In order to estimate the steric congestion of the molecule, the total energy of boat benzene was calculated by the ab initio SCF method[4] where the distances and angles of the skeleton were taken from the X-ray analysis, however, the t-butyl groups and the phosphorus atom were replaced by hydrogen atoms with normal distances (1.09Å). The flat D_{6h} benzene was calculated as an energy standard by the same method using $r_{C-C} = 1.396$ Å. The total energy of the boat benzenes was -230.327452 and -230.326862 a.u., respectively, while that of the D_{6h} benzene was -230.376113 a.u. The energy difference between the boat and the D_{6h} benzenes was 30.5 and 30.9 kcal/mol, respectively.[5] Therefore, the skeleton of the compound (1) suffers totally 61.4 kcal/mol higher energy than flat-formed benzene. Each energy difference corresponds almost to the resonance energy of a "benzene ring", indicating how strongly the t-butyl groups show ortho-effect on the molecular structure.

Taking into account only the strong interaction of the t-butyl moiety, the benzene ring could take a "chair" or an "envelope" form in terms of cyclohexane conformational analysis. Therefore, we were interested in the exclusive boat-shape formation in the compound (1), as a non-bridged compound, and the energy calculation was carried out by the same method using a model where C-C bond length is 1.396 Å, the C-H bond length is 1.09 Å, the bond angles $\angle C_1$ and $\angle C_4$ are 120°, and θ_α is 18.5° (observed X-ray value) as shown in Fig. 2.

Fig. 2



Hydrogen atoms were first assumed to be located on the perpendicular line of a triangle formed by the adjacent atoms. Energy dependence on θ_γ is shown in Table 1. The local minimum point of the total energy is shown at $\theta_\gamma = -4.83°$, where the ring is a boat shape. The difference of total energy between the envelope and the boat benzenes is not large, however, the difference of the nuclear repulsion energy is large (more than 10 kcal/mol). Therefore, the resonance-stabilized energy in the electronic structure of the boat conformation is not negligible.

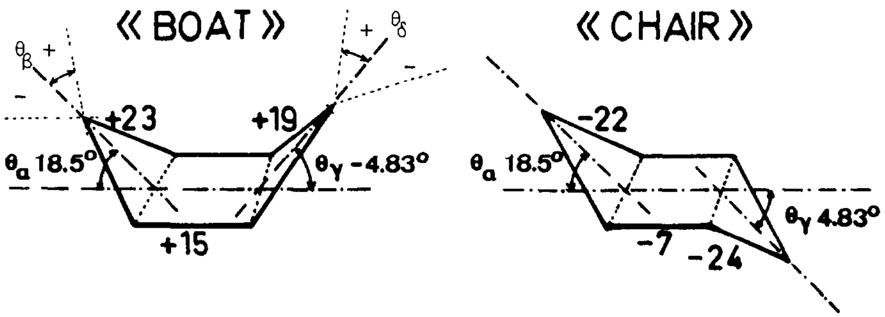
The change in the electronic structure is shown by the gross population[6] of the molecular orbitals. Figure 3 shows the gross populations between carbon atoms, where the population is listed as the difference between the boat (or chair) benzene and the envelope benzene in 10^{-4} a.u. The chemical bond of the boat benzene is stronger than the chair or envelope benzene. The other gross

Table 1

θ_γ (deg)	ΔE (kcal/mol)[a]	ΔNE (kcal/mol)[b]	IP (ev)[c]	Shape
-18.50	16.58	331.14		boat
-9.25	11.00	202.28		boat
-4.83	10.36(min)	167.67	8.85	boat
-4.63	10.39	160.64		boat
-2.31	10.59	155.77		boat
0.00	11.17	149.63	8.84	envelope
+4.83	13.53	151.96	8.79	chair
+9.25	17.03	172.09		chair
+18.50	28.36	269.86		chair

a) Total energy difference between the bent benzenes and the D_{6h} plane benzene.
b) Nuclear repulsion energy difference between the bent benzenes and the plane benzene.
c) Ionization potentials calculated by Koopmans' theorem.[7]

Fig. 3



populations (not listed in Fig. 3) are not sensitive to the geometrical variations.

The calculated ionization potential of the boat benzene is larger than that of chair benzene, indicating that the electronic structure of the boat shape is more stable than the chair or envelope shape for the external field.

In an attempt to optimize the total energy by changing the geometry of hydrogen atoms, the energy was further calculated with variable θ_β at C_1 and θ_δ at C_4 in the most stabilized "boat" skeleton ($\theta_\alpha = 18.5°$, $\theta_\gamma = -4.83°$). The energy (ΔE) is minimum (7.44 kcal/mol) at $\theta_\beta = -14.57°$ and $\theta_\delta = -3.05°$: the most stable boat benzene thus calculated carries the hydrogen atoms at C_1 and C_4 both located in "equatorial" positions.[8] As for the "chair" benzene the energy is minimum at $\theta_\beta = -15.33°$ where ΔE is 10.47 kcal/mol.

The main reason why the boat benzene is more stable than others might be due to the overlap of 1,4-electrons, and in the case of (1), the d-orbitals of the phosphorus atom might interact to a great extent to give a good overlap charge-transfer. The positive value θ_β with "axial" phosphorus atom also indicates the facile CT interaction in the compound (1).

The distorted benzene systems are known in the case of p-cyclophanes,[9,10] and the stability of the boat benzene in a multilayered [2.2]metacyclophane has been indicated by semi-empirical SCF MO calculation by using MINDO/2 approximation.[11] The energy calculations of out-of-plane deformations of aromatic rings have been preliminarily done by ab initio method by Wynberg et al.[12]

We believe that the present results are not contradictory to the X-ray analysis of the compound (1) and that the estimated large strain energy are due to the distorted benzene skeletons.

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