Arene-Arene Interactions

Organic Chemistry Seminar on February 27, 2006 was delivered by Professor Benjamin Gung, Miami University, Oxford, Ohio, on the topic "Study of Noncovalent Interactions Involving Aromatic Rings".

Question 1. Arene-Arene Interaction Basics. (20 points)

Define each of the two arene-arene interaction types. Use drawings to illustrate. Provide approximate distances to characterize the essential features of the interaction. Give approximate value for the interaction energy in kcal/mol.

Parallel Offset Arene-Arene Interaction

Arene-Arene T-Contact

Question 2. Arene Polarity. (15 points)

(a) Benzene does not have a permanent dipole moment, but it can have an induced dipole moment. Which molecular property do you need to look up in the literature if you want to make a statement as to how benzene responds to polarization?

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(b) Is the quadrupole moment of benzene permanent or induced? Explain what you believe to be the origin of the "quadrupole moment of benzene." Use illustrations as you see fit.

(c) Give an example of a quadrupolar molecule that is not a derivative of benzene.

Question 3. Arene Interactions. (15 points)

For each of the _three aggregates_, draw the structure of the aggregate as accurately as possible, describe the three most important terms of the interaction energy, and rank those three energy components with regard to their importance. [Consider: charge-charge, charge-dipole, charge-quadrupole, dipole-dipole, dipole-quadrupole, ….; charge-induced dipole, dipole-induced dipole, … temporary dipole-induced dipole (dispersion).]
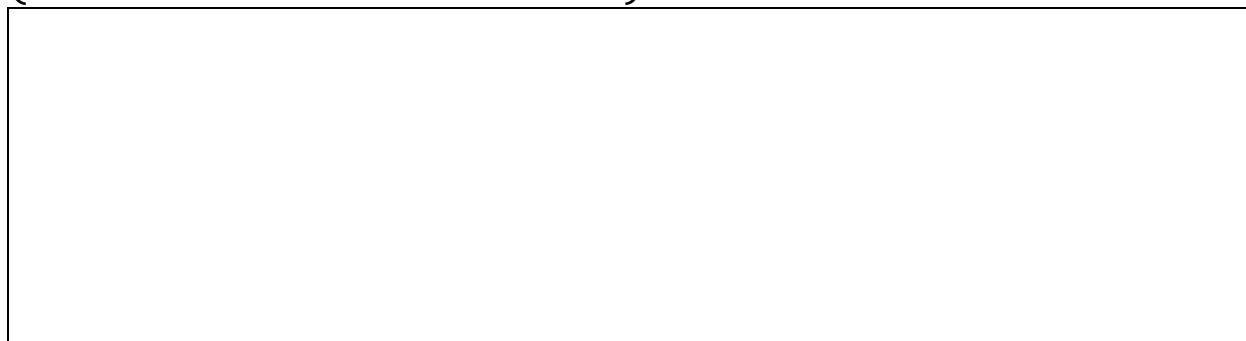
(a) The complex formed between benzene and bromonium ion.

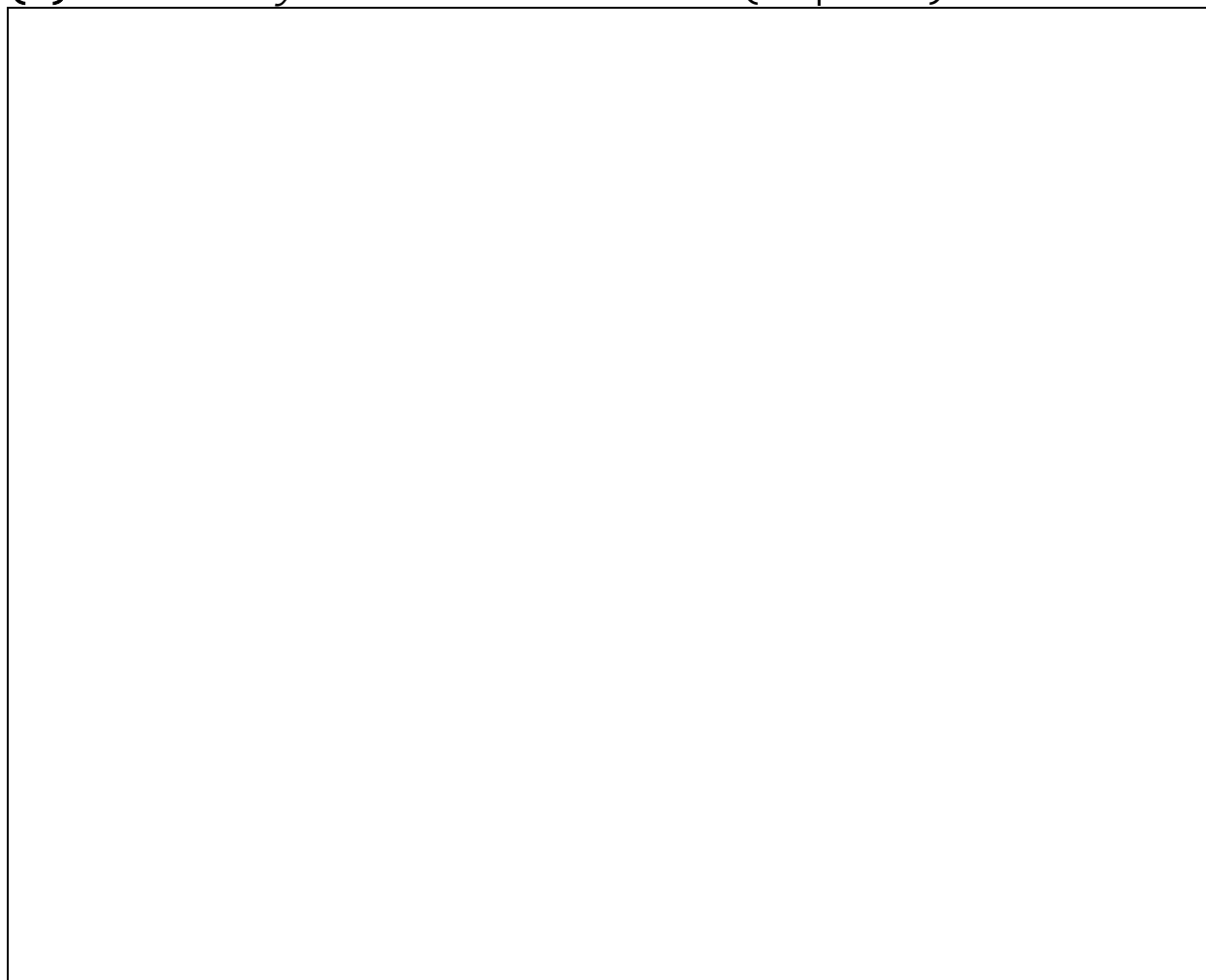**(b)** The complex formed between benzene and HBr.

(c) The complex formed between hexafluorobenzene and benzene. (Hint: This is NOT a T-contact.)

Question 4. Arene-Arene Interactions in Triptycenes. (40 p.)

The Strength of Parallel-Displaced Arene-Arene Interactions in Chloroform. Gung, B. W.; Xue, X.; Reich, H. J. *J. Org. Chem.* **2005**, *70*, 3641-3644. **Abstract:** Triptycene-derived compounds have been prepared to serve as conformational equilibrium reporters for direct measurements of arene-arene interactions in the parallel-displaced orientation. A series of such compounds bearing arenes with different substituents were synthesized, and the ratios of the *syn* and *anti* conformers were determined by variable-temperature NMR spectroscopy. The *syn* conformer allows attached arenes to interact with each other while the *anti* conformer does not. The free energies derived from the *syn/anti* ratios in chloroform range from slightly positive (0.2 kcal/mol) to considerably negative (-0.98 kcal mol) values. The interactions between the arenes bearing electron-donating groups (EDG) are either negligible or slightly repulsive, while the interactions between arenes bearing electron-withdrawing groups (EWG) are attractive. Intermediate free energy values are obtained for those compounds bearing arenes with one EDG and one EWG.

(a) Draw the *syn* and *anti* structures. (12 points)

(b) Explain what the preferred conformations are about the ester bonds [C-O and C(O)-O] and explain why each one matters. (8 p.)

(c) How do we be sure that the *syn* conformation features a "Parallel-Displaced Arene-Arene Interaction." (5 points)

(d) Suppose the free energy difference between a pair of *syn* and *anti* structures is 1.0 kcal/mol in favor of the *syn* structure. What does this number say about the "binding energy" of the intramolecular arene-arene interaction in the *syn* structure? [Hint: Start with a statement like $\Delta H > 1$ kcal/mol or $\Delta H < 1$ kcal/mol and argue your case. This is not easy and points will be given for reasonable approaches.] (15 points)

Question 5. Synthesis. (10 points)

Name the starting material that was used in Gung's synthesis.
Suggest a synthesis of this starting material.