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POSSIBLE INTERACTIONS OF CYCLOBUTADIENE WITH BY-PRODUCTS IN INERT MATRIX ISOLATION STUDIES

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The dimer and the molecular associations of cyclobutadiene with carbon monoxide, carbon dioxide, hydrogen cyanide, benzene, and phthalan have been studied theoretically by means of a 1/R expansion.

The in situ generation of cyclobutadiene in inert matrices yields by-products (which depend on the precursor used), which share the matrix cavity with the cyclobutadiene. Their mutual interaction affects their vibrational spectra, leading to difficulties in the band assignment.[1]

A theoretical study of the complexes that may be formed between cyclobutadiene and the by-products is possible, but caution is required in the interpretation of the experimental observations from the theoretical results: the latter describe the interactions existing in gas phase, while the former are influenced by the size and rigidity of the matrix cavity. In spite of these difficulties, it has been considered worthwhile to undertake such a study.

The interaction energy (ΔE) is evaluated directly by means of a 1/R expansion,

$$\Delta E = \sum\sum\{c_{ij}^{(1)}/R_{ij} + c_{ij}^{(4)}/R_{ij}^{4} + c_{ij}^{(6)}/R_{ij}^{6} + c_{ij}^{(12)}/R_{ij}^{12}\},$$

which contains terms simulating long-range electrostatic, medium-range electrostatic-induced dipole, short-range dispersive, and very-short overlap interactions, and where the summations over i,j extend to the atoms (at a distance R_{ij}) of the two interacting molecules. The coefficients have been obtained through parameterization of the results of accurate Hartree-Fock calculations[2] and tested for a number of systems (carboxylic acids, benzene, phenol, aniline, formaldehyde, etc.), with correct predictions of the stable conformations. The first step of the calculations consists of an automatic search through the configuration space; then the stable conformations are recalculated with increased accuracy. [The program is run on a Floating Point Systems array processor AP-190L, hosted by the Amdahl 470V/7 computer of the University of Alberta, and the plots of the complexes are obtained on a Tektronix T4015-1 terminal, adapted with hard copier. This program[3] may be easily adapted to any computer.] The results obtained are as follows:

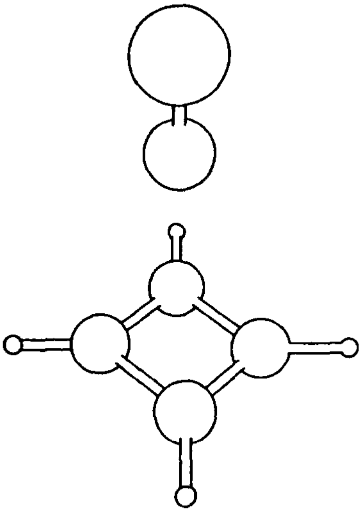

Fig. 1

(a) Interaction with carbon monoxide: The lowest minimum (ΔE = -8.4 kJ) is associated with the complex (Fig. 1) formed when the CO has approached the C_4H_4 along the axis perpendicular to the molecular plane, with the C nearer to the C_4H_4 plane (at 2.94 A). A second minimum (ΔE = -1.9 kJ) corresponds to the conformation with the CO in the C_4H_4 plane, along one of the axes through two of the H, with the O at 3.02 A from the nearest H.

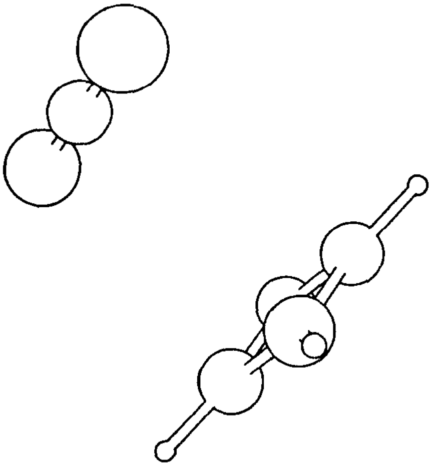

Fig. 2

(b) Interaction with carbon dioxide: Two of the three minima found are equivalent, both with an interaction energy ΔE = -3.8 kJ. They correspond to conformations with the CO_2 parallel to the C_4H_4 plane, straddling either the long (Fig. 2) or the short bonds, at distances of 3.37 and 3.39 A, respectively, from the C_4H_4 plane. The third minimum (ΔE = -0.5 kJ) results when the CO_2 approaches along the axis bisecting the short bonds, at a separation of 4.15 A between the O and the bond. [The conformation with the CO_2 approaching the C_4H_4 along the axis perpendicular to the plane has been found to be unstable. A calculation with such a conformation as starting point leads, in the automatic search, to the first conformation mentioned above.]

(c) Interaction with hydrogen cyanide: The lowest minimum (ΔE = -7.7 kJ) is obtained when the HCN approaches along the axis perpendicular to the molecular plane of C_4H_4, with the H at a distance of 2.77 A from the plane (Fig. 3). A region of shallow minima corresponds to on-plane conformations, with the N closer to the C_4H_4, pointing towards either a H (ΔE = -1.3 kJ), a short bond (ΔE = -0.8 kJ), or a long bond (ΔE = -0.6 kJ).

(d) Interaction with benzene: In the lowest energy conformation (ΔE = -3.6 kJ), the C_6H_6 straddles over the long bonds of C_4H_4, the molecular planes being perpendicular to each other; the separation between the H of C_6H_6 closest to C_4H_4 and the molecular plane of the latter is 2.93 A (Fig. 4). The second minimum (ΔE = -1.3 kJ) corresponds to a conformation where the C_4H_4 straddles over the C_6H_6, the molecular planes perpendicular to each other, with 4.59 A between the nearest long bond and the plane of C_6H_6 (Fig. 5).

(e) Interaction with phthalan: The minima correspond to the following conformations: the phthalan straddling over the C_4H_4 at an angle of 33° (Fig. 6), with the five-member ring pointing towards the C_4H_4 (ΔE = -6.0 kJ); the C_4H_4 straddling over the five-member ring (ΔE = -5.5 kJ) (Fig. 7); the C_4H_4 at a right angle to the phthalan (Fig. 8), with a H pointing towards the geminal C (ΔE = -4.7 kJ); and the phthalan straddling over the C_4H_4, with the six-member ring pointing towards it (ΔE = -4.0 kJ) (Fig. 9).

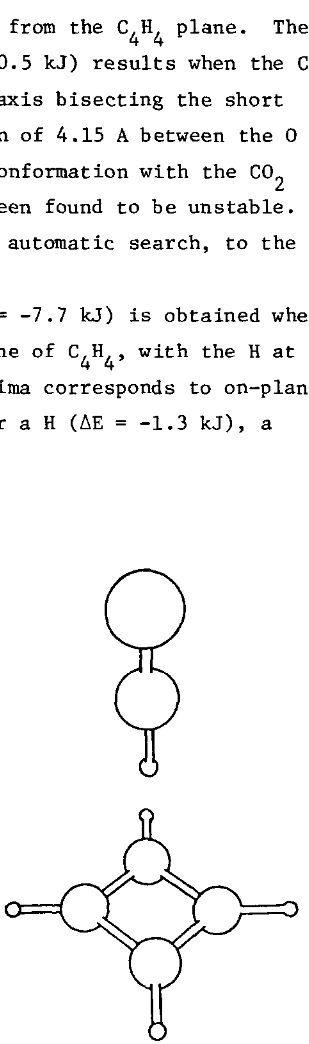

Fig. 3

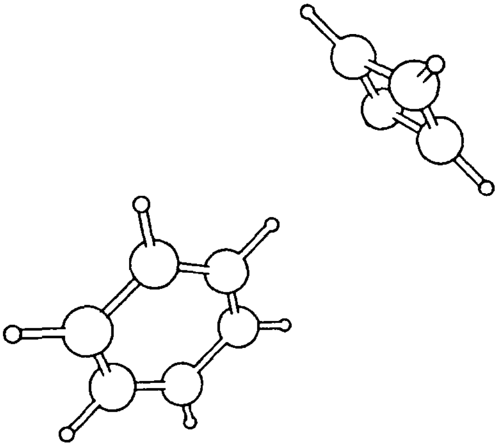

Fig. 4

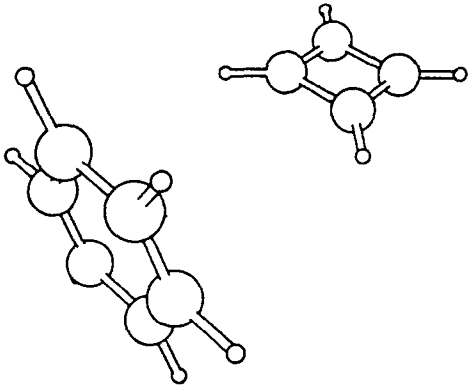

Fig. 5

Finally, for the dimer of C_4H_4, the six lowest minima correspond to two fishbone conformations (both with $\Delta E = -2.0$ kJ), differing in the relative orientations (Fig. 10), and four conformations (with $\Delta E = -1.4$, -1.2, -1.0, and -0.8 kJ) with molecular planes perpendicular to each other, differing by which bonds straddle each other, with the first one presented in Fig. 11.

The present calculations indicate that, in gas phase, stable complexes are formed with C_4H_4, although the stabilization energies are small: CO, -8.4 kJ; HCN, -7.7 kJ; C_8H_8O, -6.0 kJ; CO_2, -3.8 kJ; C_6H_6, -3.6 kJ; and C_4H_4, -2.0 kJ. The physical constraints imposed by the cavity may force the systems closer together, with the possibility of the interaction becoming repulsive. Thus, in the case of CO_2, in the most stable conformation the intermolecular separation is 3.37 A, but repulsive interactions have been reported[1] at shorter separations. Therefore, it may be worthwhile to determine the optimum conformations of such complexes within a cavity of given dimensions.

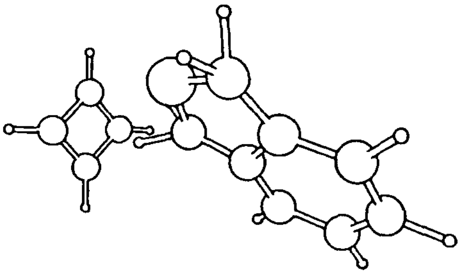

Fig. 6

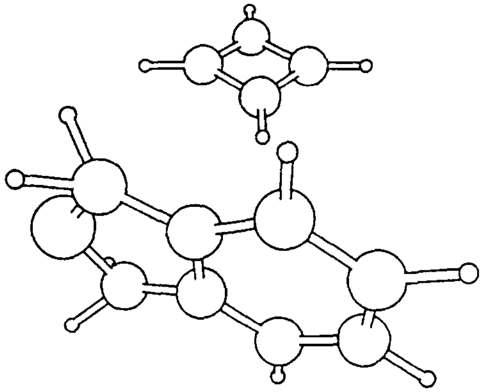

Fig. 7

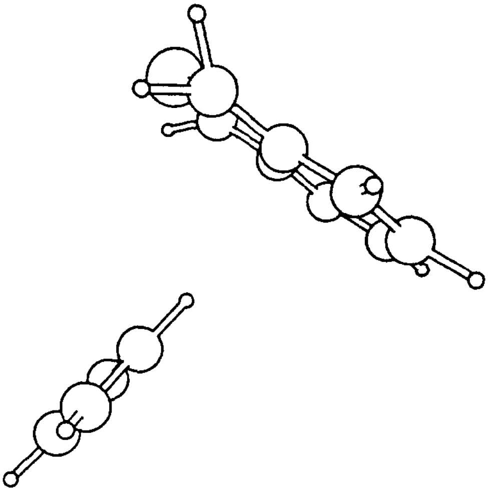

Fig. 8

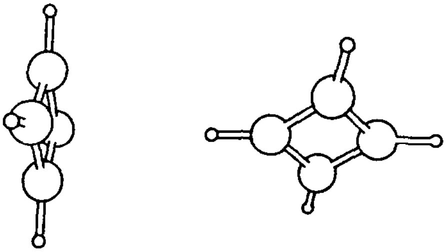

Fig. 10

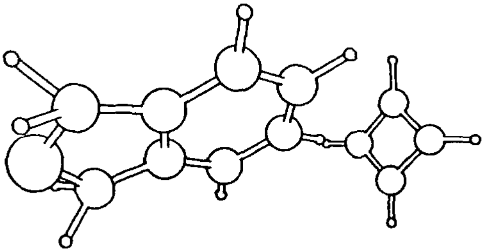

Fig. 9

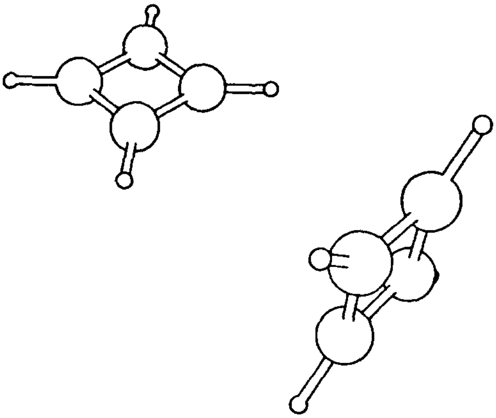

Fig. 11

References and Footnotes

1. K.B. Lipkowitz and R. Larter, Tetrahedron Letters, No. 1, 33 (1978), and references therein.
2. The parameterization was carried out for the atom-pair potentials, using the expansion coefficients of Clementi as starting point. [See, e.g., E. Clementi, 'Computational Aspects for Large Chemical Systems,' in 'Lecture Notes in Chemistry,' Springer-Verlag, Berlin (1980). The energies predicted are comparable to those obtained in SCF calculations.
3. S. Fraga, unpublished results. The program described in the text is available on request.

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