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THEORETICAL STUDY OF COMPLEXES OF CYCLOBUTADIENE WITH CARBONMONOXIDE AND CARBONDIOXIDE

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By photolysis of suitable precursors in inert matrices, cyclobutadiene can be generated and observed spectroscopically [1,2]. It has been recognized only recently, however, that some features in the IR spectra obtained are not due to cyclobutadiene [3,4]; e.g. in the photolysis of Corey's lactone, the IR band at 653 cm^{-1} originally assigned to cyclobutadiene corresponds to the bending vibration of carbondioxide which is formed as a byproduct. To account for the observed splitting and shift of this band compared to free carbondioxide, the existence of cyclobutadiene complexes with ligands such as carbondioxide has been postulated [3].

In the present communication, the stability of such complexes with carbonmonoxide and carbondioxide is investigated by single-determinantal MNDO [5] and MINDO/3 [6] calculations, with complete optimization of molecular geometries within a given symmetry by a modified Davidon-Fletcher-Powell algorithm [7]. Since the MNDO and MINDO/3 results are fairly similar, we shall discuss them together.

For the cyclobutadiene/carbondioxide system, several orientations were considered. Figure 1 shows the results for two symmetrical approaches, the CO_2 molecule being either in the C_2 axis perpendicular to the ring (approach a) or in a plane parallel to the ring, with its carbon atom in the C_2 axis [8] (approach b); both approaches lead to strongly repulsive potentials, with no trace of a local minimum [9]. Likewise, unsymmetrical orientations do not yield any stabilization, and geometry optimizations without constraints always result in dissociation. Our scan of the potential surface thus indicates that there is no local minimum for a complex between cyclobutadiene and carbondioxide [10].

A different situation is encountered for the cyclobutadiene/carbonmonoxide system [11]. Starting from a rectangular cyclobutadiene structure with the CO molecule in the C_2 axis perpendicular to the ring, geometry optimization under im-

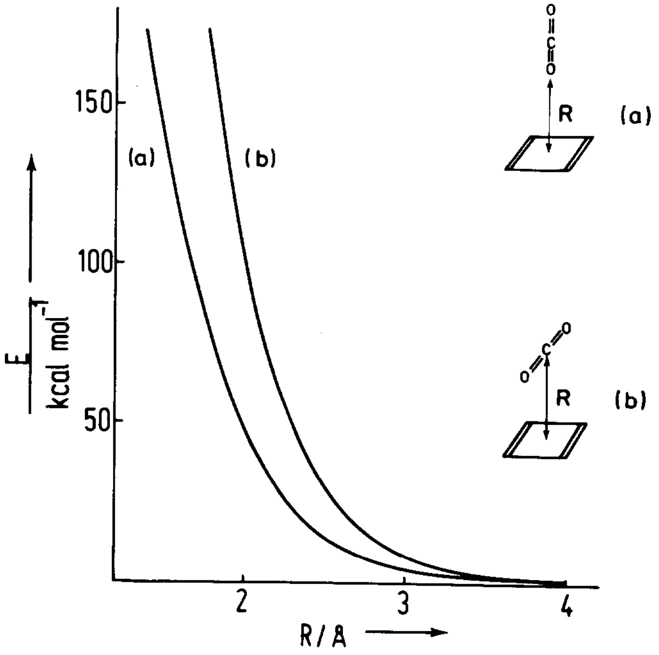

Figure 1. MNDO energies E for two approaches of carbondioxide to cyclobutadiene.

posed C_{2v} symmetry leads to a stable C_{4v} structure with a square cyclobutadiene moiety (see Figure 2). This C_{4v} species is a typical π-complex [12], with cyclobutadiene acting as donor and carbonmonoxide as acceptor. According to MNDO, there is a charge transfer of -0.138 formal charges, mainly from the degenerate π -MOs of cyclobutadiene to the π^*-MO of carbonmonoxide. As a consequence, a square geometry for the cyclobutadiene ring is favored over a rectangular one, whereas the CO bond is lengthened by 0.056 Å and its vibrational frequency is reduced by 243 cm^{-1} (MNDO) compared to free carbonmonoxide. The energy of the π-complex relative to the isolated molecules is calculated to be +53.4 kcal/mol by MNDO and +0.6 kcal/mol by MINDO/3 [13]; these values should be regarded as upper and lower bounds since the stability of highly bridged structures is usually underestimated by MNDO and overestimated by MINDO/3.

Having established the π-complex as a local minimum under C_{4v} symmetry, the cyclobutadiene/carbonmonoxide system was reinvestigated without imposing any symmetry constraints. Starting from an unsymmetrical geometry close to that of the π-complex, the optimization procedure does not lead to the π-complex, but to

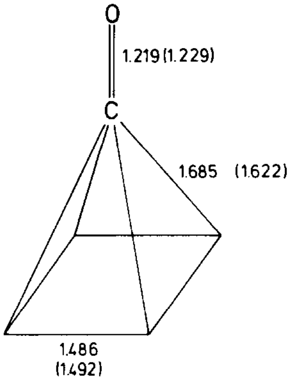

Figure 2.

Optimized MNDO geometry for the π-complex (MINDO/3 values in brackets). Bond lengths in Å.

bicyclo[2.1.0]pentenone. This suggests that the π-complex is not a true minimum on the C_4H_4CO potential surface. Diagonalization of the force constant matrix for the π-complex indeed shows the existence of two degenerate negative eigenvalues [14], the transition vectors corresponding to the motion of the CO unit across the ring. The π-complex between cyclobutadiene and carbonmonoxide thus constitutes the "hilltop" for CO-scrambling in bicyclo[2.1.0]pentenone.

Our calculations lead to the conclusion that there are no complexes of cyclobutadiene with carbondioxide or carbonmonoxide which would correspond to minima on the respective potential surfaces. It should be noted, however, that our calculations refer only to the gas phase. The observed splittings and shifts in the IR spectra [3,4] are then probably due to matrix effects, i.e. interactions between cyclobutadiene and carbondioxide/carbonmonoxide in the matrix cavity where they are formed together [15].

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References and Footnotes

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