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$P_\sigma P_\sigma$ Interactions in Organic Molecules 1.
π-Face Bonding of Cyclobutadiene.

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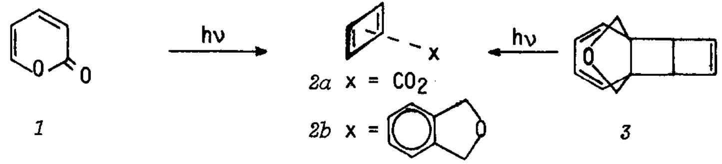
Highly reactive chemical species can be spectroscopically observed for extended periods of time by trapping them in an inert matrix.[1] Thus the method of matrix isolation has been used to study cyclobutadiene which otherwise forms isomeric dimers or undergoes chemical reaction. Typically, a suitable precursor molecule is trapped in a matrix and photolyzed so that cyclobutadiene is generated in situ. Accompanying C_4H_4, though, are several by-products (depending on starting material) which are extruded into the same matrix cavity as cyclobutadiene. Until recently, these compounds have been ignored but several papers have suggested that the assignment of vibrational bands in C_4H_4 has been obscured by these waste materials.[2]

Corey's lactone, (*1*), which serves as a convenient progenitor to cyclobutadiene, extrudes CO_2 and presumably forms a complex (*2a*). Likewise, Masamune has shown that (*3*) produces cyclobutadiene and phthalic anhydride which could give rise to a species like (*2b*).



In this communication we ask whether a pi complex between cyclobutadiene and carbon dioxide is feasible and if so what the intermolecular geometry looks like. To begin with, perturbation theory suggests the possibility of net stabilization between C_4H_4 and CO_2 (figure 1). There are several distinct geometries for interaction but we will focus our attention on only those where x approaches cyclobutadiene from the pi face. Three geometries considered are shown in figure 1. Geometry a has the CO_2 bond axis parallel to the hydrocarbon plane and parallel to the long axis of D_2h cyclobutadiene. Geometry b is identical except that the CO_2 axis is parallel to the short axis of cyclobutadiene. Geometry c has the CO_2 bond axis perpendicular to the hydrocarbon plane. In all three cases the CO_2 carbon is on the z

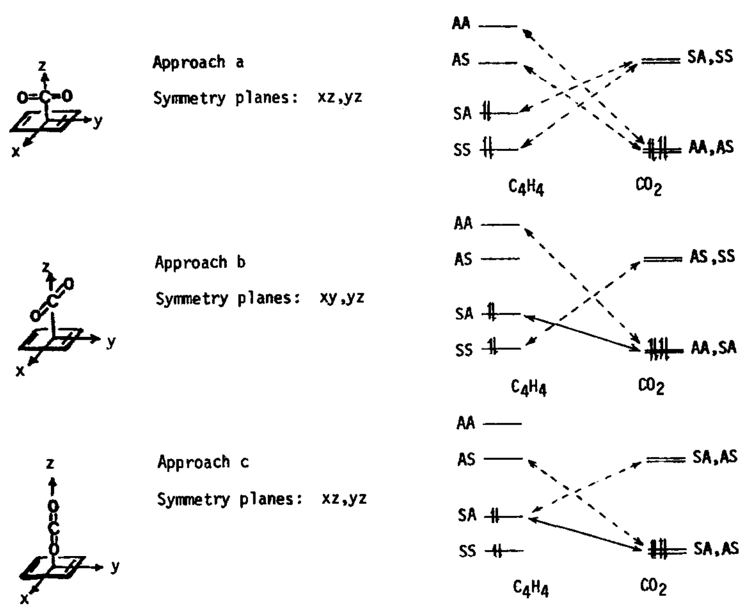


Figure 1 - Qualitative interaction of C_4H_4 and CO_2

axis. The four electron destabilizing interactions (solid arrows) could be compensated for by the two electron stabilizing interactions (broken arrows) arising from mixing with low lying empty orbitals of appropriate symmetry. Though one may anticipate some stabilization of the complex, the magnitude of this interaction is questionable.

To investigate whether a net stabilization exists or not, semiempirical calculations were performed on the three geometries for each complex. CNDO/2[3] total energies plotted against intermolecular distances show distinct minima (figure 2), and in most instances the magnitudes of these minima are unusually large, indicating an unreliable calculation.[4] Indeed, it has been documented that CNDO and INDO closed shell restricted Hartree Fock methods are unable to account for certain nonbonded interactions.[5a,b]

Though other semiempirical calculations may provide better results,[5b,6] we felt it necessary to take into account all interactions and proceeded with ab initio calculations. A flexible basis is desirable but due to the large number of integrals to evaluate, calculations were done using the minimal STO-3G basis set. Becuase of its use of molecular symmetry properties via the Elder formalism, the ab initio program Phantom[7] was used. Figure 3 presents the change in total energy as a function of intermolecular separation.

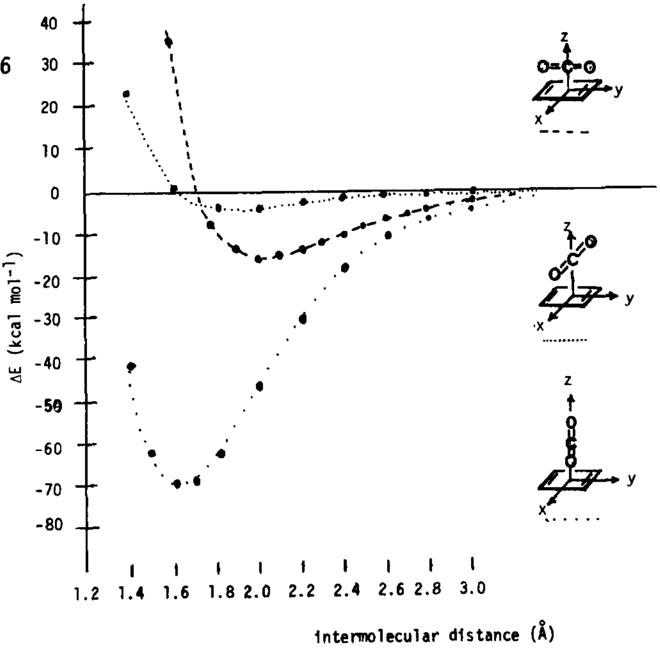


Figure 2 - CNDO Total Energies

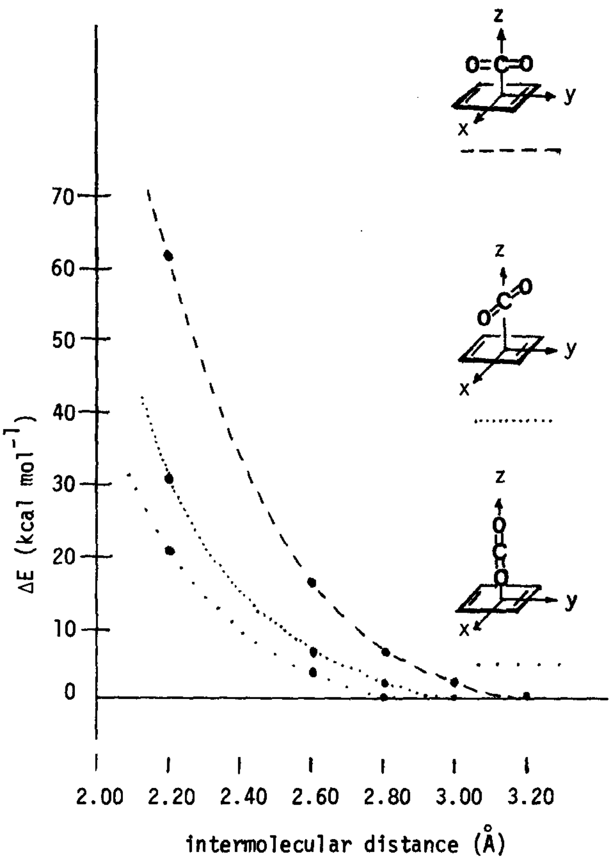


Figure 3 - Total ab initio energy as a function of intermolecular distance.

In all three geometries there exists a repulsive interaction at approximately 3.20 Å; however, the degree of destabilization depends upon the geometry of approach. Apparently the most stable arrangement of rectangular cyclobutadiene and carbon dioxide is the geometry in which the CO_2 bond axis is perpendicular to the cyclobutadiene plane.

Maier first suggested that the 653 cm^{-1} absorption observed from photolysis of 1 not be assigned to cyclobutadiene but rather to CO_2 functioning as a ligand.[2a] That is to say, either there are two different environments for CO_2 (intimate pair or host separated pair)[2b] or the degeneracy of the asymmetric CO_2 bending mode is lifted by the presence of cyclobutadiene.[2a,b]

If this latter explanation holds, we suggest that the geometry of the complex in the argon cavity be a minimum energy complex and represented by the structure where CO_2 is parallel to the C_4H_4 plane and perpendicular to the long axis of rectangular cyclobutadiene (approach b) depicted by Krantz.[8] At large intermolecular distances, the distinction between parallel and perpendicular alignments are insignificant, viz. 4 kcal difference in total energy at 2.80 Å. At very close distances, conceivable in a rigid matrix, there becomes a very significant difference between the parallel and perpendicular geometries, viz. 21 kcal difference in total energy at 2.40 Å. One may expect that if the splitting arises from the lifting of degeneracy by neighboring cyclobutadiene it is a function of the size and rigidity of the matrix cavity. Cyclobutadiene interactions with carbon monoxide, hydrogen cyanide and benzene are currently under investigation and will be reported elsewhere.

Footnotes and References

1. a) H. E. Hallam, ed. "Vibrational Spectroscopy of Trapped Species," Wiley, London, 1973.
   b) B. Meyer, "Low Temperature Spectroscopy," American Elsevier, New York, N.Y., 1971.
   c) S. Cradock and A. J. Hinchcliffe, "Matrix Isolation, A Technique for the Study of Reactive Inorganic Species," Cambridge University Press, Cambridge, 1975.

2. a) G. Maier, H. Hartan and T. Sayrac, Angew. Chem. Int. Ed. Engl., 15, 226 (1976).
   b) R.G.S. Pong, B.-S. Huang, J. Laureni and A. Krantz, J. Am. Chem. Soc., 99(12), 4153 (1977).

3. a) Q.C.P.E. Program #141, Indiana University, Bloomington, Indiana.
   b) ΔE is defined as the difference in energy between cyclobutadiene-carbon dioxide at infinite separation and cyclobutadiene-carbon dioxide at finite distance. Intermolecular distance for approach a and b is the distance between the CO_2 bond axis and the cyclobutadiene plane; intermolecular distance for approach c is the distance between the nearest carbon dioxide oxygen and the cyclobutadiene plane.
   c) Carbon dioxide bond length is 1.162 Å. D_{2}h cyclobutadiene bondlengths are: C-C 1.33 Å, 1.52 Å; C-H 1.10 Å.

4. CNDO/2 calculation of cyclobutadiene and carbon monoxide have minima similar to those shown in figure 2 but much deeper. In one case a minimum of $\sim$370 kcal mol^{-1} was found. Unpublished results of K.B. Lipkowitz.

5. a) For leading references see A.R. Gregory and M.N. Paddon-Row, J. Am. Chem. Soc., 98:24, 7521 (1976).
   b) D.B. Chestnut and P.E.S. Wormer, Theor. Chim. Acta (Berl.), 20, 250 (1971).

6. The perturbative procedure, PCILO, appears to better adapt to the study of molecular complexes than CNDO. See for example R. Lochman and H.J. Hofmann, Int. J. Quant. Chem., 11, 427 (1977) and R. Arnaud, D. Faramond-Baud and M. Gelus, Theor. Chim. Acta (Berl.), 31, 335 (1973).

7. Q.C.P.E. Program #241, Indiana University, Bloomington, Indiana.

8. In view of the results shown in figure 3, we suggest that carbon dioxide not be considered a *ligand* as proposed by Maier (ref 2a) and that Krantz is correct in suggesting the CO_2 splitting could result from a repulsion rather than an attraction between cyclobutadiene and carbon dioxide (footnote 10, ref 2b).

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