

$p_{\sigma}p_{\sigma}$ Interactions. 2. π Face Bonding in Cyclobutadiene

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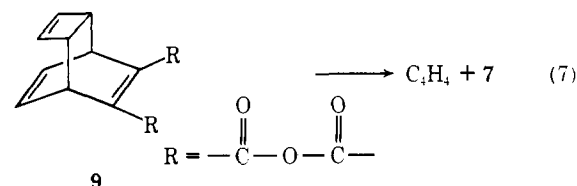
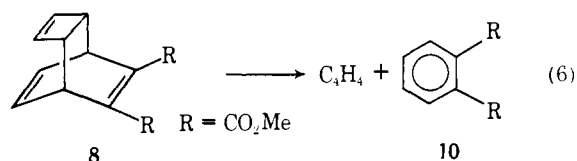
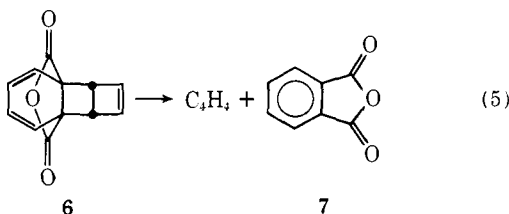
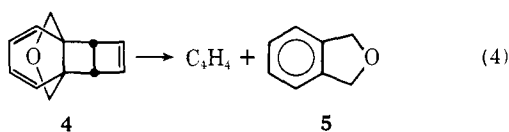
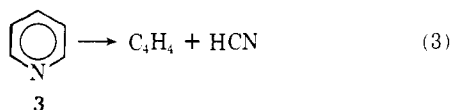
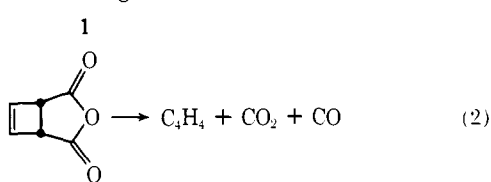
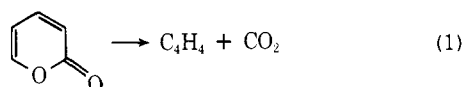
Abstract: The π face bonding of rectangular singlet cyclobutadiene with carbon monoxide, hydrogen cyanide, and benzene is investigated. CNDO/2 total energies for several possible intermolecular geometries are found to be unreliable when compared to minimal basis ab initio results. A long-range attractive interaction between cyclobutadiene and carbon monoxide is found for geometry III but all other complexes are unstable. Rotational interconversion from one geometry to another is considered for several complexes.

Introduction

While metal-complexed and sterically congested cyclobutadienes are stable and quite well characterized, the parent hydrocarbon is not. In fact, its geometry and electronic configuration may be considered a chemical conundrum rivaled only by the classical-nonclassical carbonium ion controversy. One thing for certain about this cyclic member of the C_nH_n family is that, although it has a very short lifetime, it can be studied in a matrix at low temperature.¹

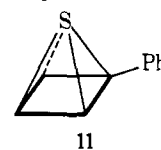
Typically a suitable precursor is trapped in an inert matrix. Photofragmentation yields cyclobutadiene that may then be leisurely studied. Unfortunately, though, several byproducts are extruded into the matrix cavity that tend to obfuscate assignment of IR absorption bands. Until recently these side products have been completely ignored, but Maier² has published a communication in which it was suggested that earlier interpretations of IR data needed modification as a consequence of cyclobutadiene π face interactions with carbon dioxide. This was independently confirmed by Krantz³ and there is reason to believe that any spectral assignments made in a matrix be taken cum grano salis in light of the potential complexing ability of cyclobutadiene.

Only a few photolabile precursors of cyclobutadiene are known. α -Pyrone (**1**) produces the desired hydrocarbon along



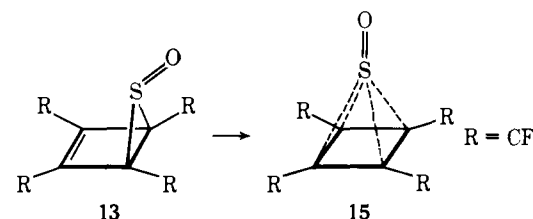
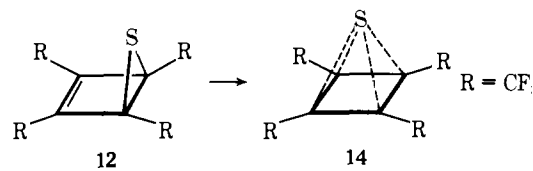
with carbon dioxide (eq 1).⁴ Photofragmentation of anhydride **2** produces C_4H_4 , carbon dioxide, and carbon monoxide (eq 2).⁵ Photolysis of pyridine produces in low yield cyclobutadiene and hydrogen cyanide (eq 3).^{4d} The more complex parent structures, **4**, **6**, **8**, and **9**, are likewise converted to cyclobutadiene and the corresponding byproducts (eq 4-7),⁶ all of which contain an aromatic chromophore.

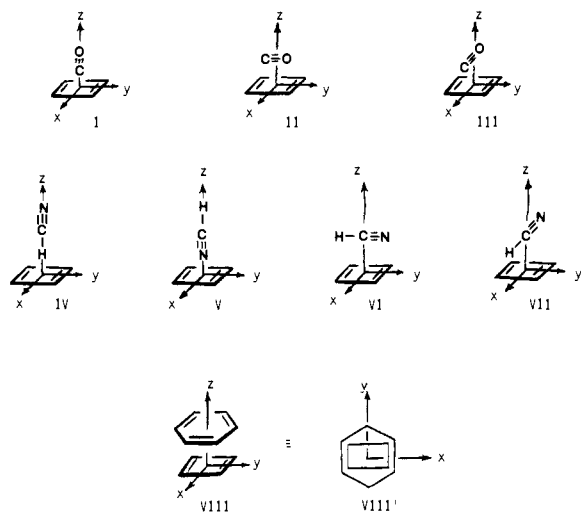
Other cyclobutadiene complexes have been proposed as high-energy transients during molecular rearrangement. For example, the reaction of phenylthiophenes in glow discharges show that 2-phenylthiophene will isomerize to 3-phenylthiophene and vice versa. One postulated intermediate is structure



11.⁷ This was also suggested as a reasonable intermediate to explain ¹³C labeling patterns during electron impact.⁸

The automerizations of Dewar thiophene **12** and the corresponding exo *S*-oxide, **13**, have been studied. The exact mechanism of site exchange is unknown but a concerted, pseudopericyclic process involving peripheral migration of sulfur was tentatively favored over a transannular migration that would result in **14** and **15** as transient species.⁹ Since then



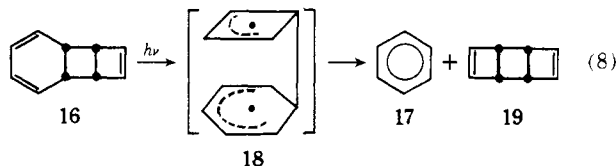


- I. The CO bond is perpendicular to the cyclobutadiene plane.
- II. The CO bond is parallel with the cyclobutadiene plane and parallel with its long axis.
- III. The CO bond is parallel with the cyclobutadiene plane and perpendicular to its long axis.
- IV. HCN is perpendicular to the cyclobutadiene plane and directly on the z axis.
- V. HCN is perpendicular to the cyclobutadiene plane and on the z axis.
- VI. HCN is parallel to the cyclobutadiene plane and parallel with its long axis.
- VII. HCN is parallel to the cyclobutadiene plane and perpendicular to its long axis.
- VIII. C_6H_6 is parallel to the cyclobutadiene plane and rotated along the z axis as shown in VIII'.

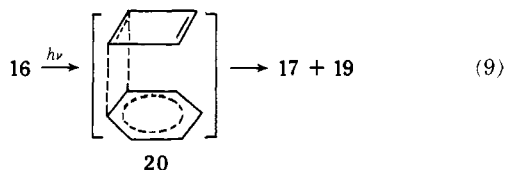
Figure 1. The intermolecular geometries of rectangular cyclobutadiene with carbon monoxide, hydrogen cyanide, and benzene.

an enlightening study of this allylic rearrangements suggested that square pyramidal structures **14** and **15** are indeed quite acceptable rearrangement intermediates.¹⁰

Finally the tremendous amount of work directed toward understanding the $C_{10}H_{10}$ thermal and photochemical hypersurfaces has shown that photolysis of **16** results (along with other products) in a substantial quantity of benzene (**17**) and cyclobutadiene dimer **19**. One suggestion was that diradical **18** serves as a likely precursor to these products (eq 8).¹¹ An



alternative source of **17** and **19** is the symmetry-allowed excited state [2 + 2] cycloreversion reaction as depicted in eq 9.¹¹



Other cyclobutadiene and substituted cyclobutadiene complexes have been mentioned by Maier.¹

Our interest in $p_\sigma p_\sigma$ bonding led us to investigate the π face bonding of the parent cyclobutadiene and carbon dioxide.¹² In that study we suggested that a π complex between C_4H_4 and CO_2 is not feasible and the "complex" observed by Maier was a result of CO_2 being artificially constrained to lie over the cyclobutadiene by the matrix. In fact, a rather severe repulsive interaction appears to exert itself at an intermolecular distance of 2.4–2.6 Å regardless of how CO_2 approaches the π plane. Furthermore, it was indicated that the geometry of the complex in the matrix cavity is a minimum energy complex that may

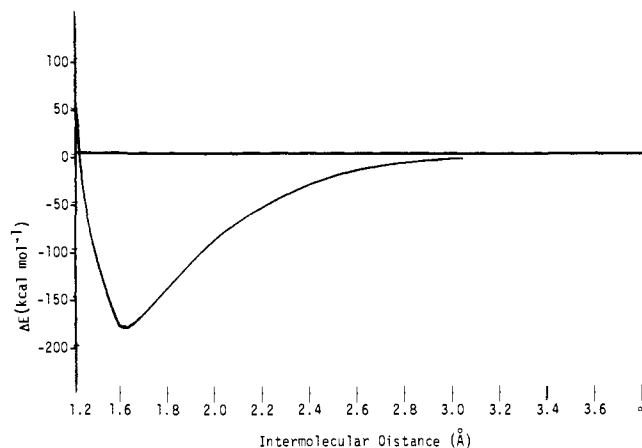


Figure 2. Total energy of a benzene-cyclobutadiene complex (geometry VIII) calculated by CNDO/2.

be represented by the structure in which CO_2 is parallel to the C_4H_4 molecular plane and perpendicular to the long axis of rectangular cyclobutadiene. In this paper we wish to discuss the π bonding abilities of cyclobutadiene with other molecules, particularly carbon monoxide, hydrogen cyanide, and benzene.

Results

The method of investigation is to study the total energy of cyclobutadiene and its artificial ligand as a function of intermolecular distance using standard quantum mechanical techniques. Two approaches to this problem are tried: a semiempirical technique (CNDO/2) and ab initio calculations. In this paper, cyclobutadiene is treated as a rectangular singlet species with a geometry previously described.¹² Bond lengths for carbon monoxide, hydrogen cyanide, and benzene are experimentally determined.¹³ The original CNDO/2 parameters were used unchanged.¹⁴ For the ab initio calculations, a minimal STO-3G basis set was implemented¹⁵ and in all cases at least one, and, where appropriate, two symmetry planes were utilized to reduce computational times. All species calculated individually (infinite intermolecular separation) quickly converged using the program PHANTOM.¹⁶ Evaluation of the complexes tended to oscillate in the SCF calculation but could be made to converge in less than 50 iterations by applying a density matrix averaging of 0.25.

As in the case of carbon dioxide several geometries were used.¹² These are labeled I–VIII in Figure 1. In all cases the center of cyclobutadiene is on the origin. For all geometries where the "ligand" is perpendicular to the cyclobutadiene plane the intermolecular distance is the distance from the origin of the Cartesian coordinate system to the atom closest to C_4H_4 . The plot of total energy vs. intermolecular distance for benzene-cyclobutadiene calculated with the semiempirical program is shown in Figure 2. The same system calculated ab initio is shown in Figure 3. Energies for CO -cyclobutadiene computed with CNDO/2 and ab initio are presented in Figures 4 and 5, respectively. Ab initio values for HCN -cyclobutadiene are in Figure 6.

Discussion

I. Semiempirical Results. The semiempirical evaluation of D_{6h} benzene with D_{2h} cyclobutadiene shows a tremendous stabilization at an intermolecular distance of 1.60 Å (Figure 2). Electron transfer from one ring to the other is not evident, but rather, a total electron reorganization within each ring has taken place. Perusal of the density matrix at the minimal energy geometry indicates a structure closely resembling biradical **21**. This intermediate is known and irreversibly rear-

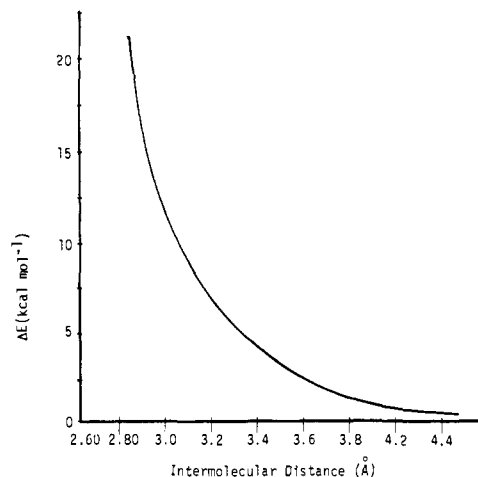


Figure 3. STO-3G evaluation of total energy of complex VIII as a function of intermolecular distance.

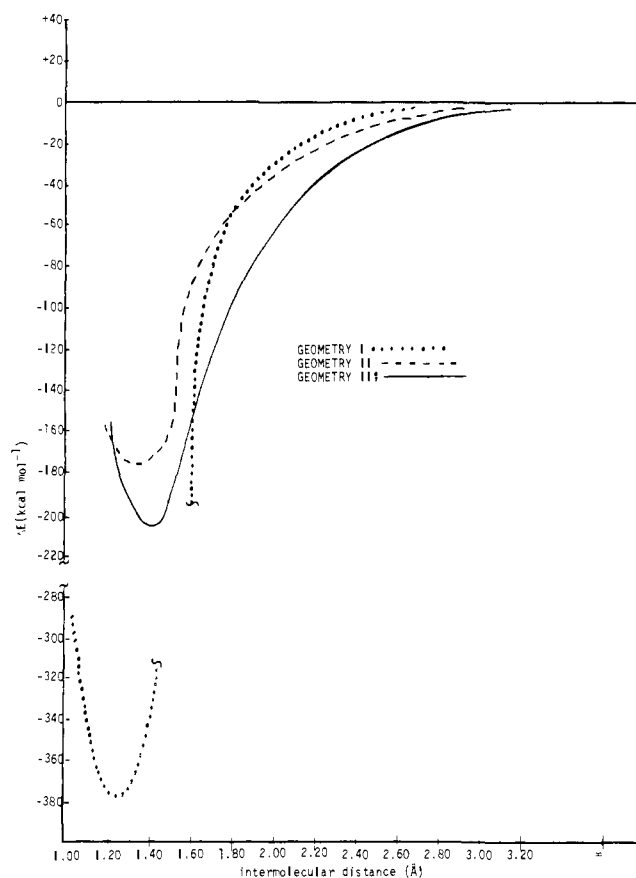
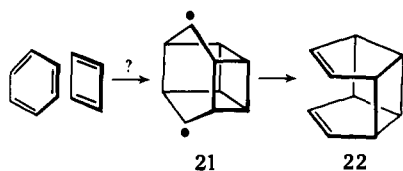


Figure 4. Total energy of several cyclobutadiene-carbon monoxide complexes calculated with CNDO/2.



ranges to hypostrophene (**22**).¹⁷ While the thought of benzene and cyclobutadiene giving rise to hypostrophene is tempting, this suggestion is not tenable in light of the unreasonably large calculated interaction energy. Indeed, CNDO/2 has been known to overestimate certain interactions, particularly those involving π complexes.¹⁸

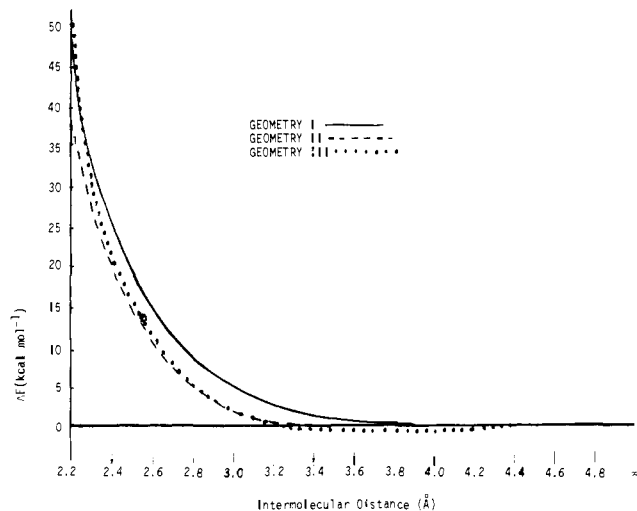


Figure 5. STO-3G evaluation of total energy for several cyclobutadiene-carbon monoxide complexes.

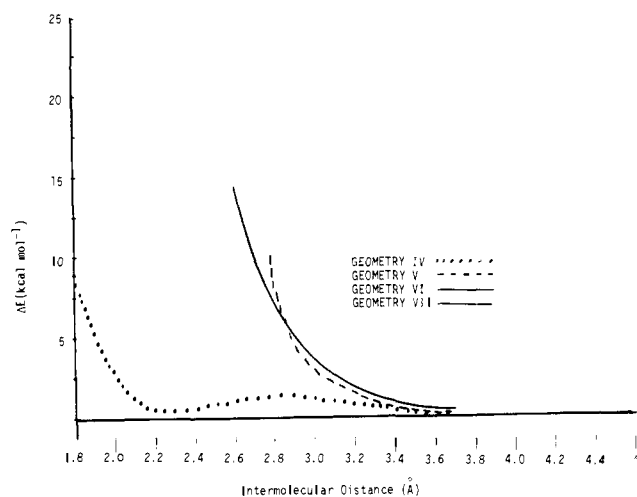


Figure 6. STO-3G total energies for several cyclobutadiene-hydrogen cyanide complexes.

The semiempirical calculations of cyclobutadiene and carbon monoxide give energy minima between 1.20 and 1.40 Å depending on geometry (Figure 4). These minima are several orders of magnitude larger than might be expected. Since we had originally intended to investigate relatively large organic molecules interacting with cyclobutadiene we initiated this study with approximate molecular orbital methods. It appears, though, that CNDO/2 is unreliable for this study and we have abandoned this approach.

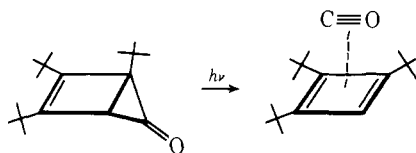
II. Ab Initio Results. The poor CNDO/2 results are, in part, a consequence of neglecting too many repulsive interactions (thus overestimating the attractive ones). This can be rectified with a minimal basis ab initio approach. Contrary to the CNDO results, all cases studied indicate a repulsive interaction that generally becomes severe at an intermolecular separation of 3.20–3.00 Å. SCF theory never predicts van der Waals binding since the latter is due to correlation effects. Semiempirical schemes such as CNDO do not give this effect either. Hence the calculation presented here eliminates only chemically bound complexes, and not van der Waals complexes.

In a previous communication¹² we investigated the interactions of cyclobutadiene and carbon dioxide. Three distinct geometries were studied, all of which displayed repulsive interactions. We concluded that the cyclobutadiene complex should exist as a minimal energy complex and, for reasons discussed by Krantz,³ suggested the geometry where the car-

bon dioxide bond axis is parallel with the hydrocarbon plane and perpendicular to the long axis of the rectangle.

In the case of carbon monoxide-cyclobutadiene, the energies of configurations II and III are virtually indistinguishable and both show less of an adverse interaction than geometry I between 2.60 and 3.40 Å (Figure 5). It would seem that one of these two (II and III) and possibly both geometries may exist in a matrix with a rectangular cyclobutadiene. Alternatively, these two geometries may be interconverting via carbon monoxide free rotation about the z axis. Indeed, the calculated change in energy upon 15° incremental rotation from geometry III to II at 3.2 Å intermolecular separation reaches a maximum at 60° rotation. This maximum is less than 0.5 kcal mol⁻¹, which indicates virtually free carbon monoxide rotation. The intermolecular separation of 3.2 Å was arbitrarily chosen but similar calculations at other distances qualitatively demonstrate the same behavior of showing an energy maximum for diagonal geometries. Interconversion from II to III via geometry I is not reasonable since a barrier of 2-4 kcal mol⁻¹ exists between either II and I or III and I. Of course if the matrix is very tight, forcing the carbon monoxide and cyclobutadiene within 2.40 Å of one another, this interconversion appears more reasonable.

At long range there is a slight attractive interaction (<0.50 kcal mol⁻¹) between 3.4 and 4.4 Å for geometry III. While this may be a dipole-induced-dipole effect we see no attraction between carbon monoxide and cyclobutadiene for the other geometries. Nevertheless, there is experimental evidence that carbon monoxide complexes to tri-*tert*-butylcyclobutadiene in an argon matrix as a result of 313-nm photofragmentation of the appropriate bicyclic cyclopentenone.¹⁹ Whether this effect can be seen with the parent cyclobutadiene is not known.



The interaction of cyclobutadiene with hydrogen cyanide is also a function of geometry. As in the case of carbon monoxide complexes II and III, the energies of hydrogen cyanide complexes VI and VII are indistinguishable. The least favorable geometry is V in which the electronegative nitrogen is pointed directly into the annulene π face. The most favorable configuration is IV where the hydrogen is pointed into the cyclobutadiene π face. It is this arrangement which has a distinct stabilizing effect between 2.8 and 2.1 Å. As yet, we do not fully understand the origin of this attraction.

The question of whether one or more of the hydrogen cyanide geometries exist in the matrix and whether there is a rapid conversion from one form to another merits attention. Disregarding geometry V (since it is the most unstable complex at short distances) we are left with IV, VI, and VII, of which IV is by far the most appealing. As in the case of II-III interconversion, VI and VII may readily interconvert since incremental rotation of hydrogen cyanide about the z axis (which transforms VII into VI) involves a small energy barrier. This barrier is approximately 0.5 kcal mol⁻¹ at an intermolecular distance of 2.6 Å and, in essence, hydrogen cyanide may freely rotate above the annulene π plane. As in the case with carbon monoxide, this intermolecular distance was arbitrarily chosen. Rotational barriers calculated at different distances, however, qualitatively display the same behavior. Whether complexes VI and VII would exist at all is highly unlikely in view of the minimal repulsive energy associated with IV.

The interaction of benzene and cyclobutadiene is shown in Figure 3. Unlike the exciting, albeit unsatisfactory, semiempirical results, a smooth repulsion of the two planar molecules

is evident. Rotation of benzene about the z axis was not considered nor were any other geometries.

Conclusions

π face bonded cyclobutadienes have only recently been investigated. Experimentally there is some evidence for the by-products of photofragmentation to form complexes with cyclobutadiene and with tri-*tert*-butylcyclobutadiene.^{1,19} In this paper we investigated the π face bonding of cyclobutadiene with carbon monoxide, hydrogen cyanide, and benzene, using semiempirical and minimal basis ab initio techniques. The CNDO/2 results were found to be very poor representations of intermolecular interactions by virtue of their overestimating attractive forces.

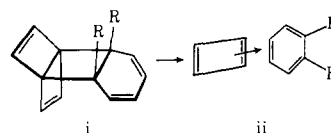
The ab initio calculations all show repulsive interactions except at long range for carbon monoxide. The results suggest that benzene, carbon monoxide, and hydrogen cyanide should not be considered ligands of cyclobutadiene. If anything, these "ligands" appear to be artificial in that the rigid matrix may be holding them together. For the carbon monoxide complex, geometries II and III are the most stable. Interconversion of II and III requires minimal energy and the C≡O may be thought of as a species that is freely rotating parallel to the annulene π plane. The most stable complex for hydrogen cyanide is geometry IV. In this configuration the approach of HCN toward the annulene π plane shows a distinct attraction between 2.8 and 2.1 Å. Only one geometry for the benzene complex was studied and it was uneventfully repulsive in character.

In general, the ab initio calculations suggest that cyclobutadiene interactions with benzene, carbon monoxide, hydrogen cyanide, and carbon dioxide¹² at close range are destabilizing. It is appropriate that the magnitude and direction of IR shifts for complexed and free "ligands" is critical to these interpretations and should be carefully scrutinized.²⁰ One further problem concerns the shape of cyclobutadiene in the presence of the aforementioned byproducts. If the matrix is reasonably tight and not permitting the byproducts to diffuse away upon photofragmentation, one can expect the annulene to react to this kick in the π face by altering its geometry. The question of how these perturbations influence the geometry of cyclobutadiene merits attention and is being studied.²¹

Acknowledgments. We wish to thank Research Corporation for supporting this investigation. The correspondence with Professor Maier is greatly appreciated as is the interest shown by Drs. A. Szabo, M. Marsh, D. Boyd, and B. Hermann.

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- (21) Since this work was completed, a communication has appeared confirming the destabilizing effect of C₄H₄ with carbon dioxide as we had originally reported in ref 12. Also reported is an energy minimum for cyclobutadiene with carbon monoxide. These results were obtained using MNDO type calculations and suggest that MNDO mimics ab initio results quite well. A. Schweig and W. Thiel, *Tetrahedron Lett.*, 1841 (1978).

Quantum Mechanical Partitioning of the Energies of Polypeptides. Conformational Study of Polyglycine

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Abstract: The total energy of a polypeptide is partitioned into the interaction energies between pairs of residues. The interactions between adjacent residues are evaluated by quantum mechanical methods. An empirical hydrogen bond potential based on the quantum mechanical interaction between amide units is formulated and used to calculate the interaction energy between nonadjacent residues. This treatment is used to study regular helical conformations of an isolated single strand of polyglycine. The α helix is found most stable while the 3_{10} and 2_7 helices are also low-energy structures. The calculated results are compared to those obtained via classical partitioning procedures as well as experiment.

I. Introduction

Reliable means of evaluating energies of proteins are needed for predictive and interpretative studies of three-dimensional structure. Although quantum mechanical procedures have yielded results in excellent agreement with experiment when applied to many chemical systems, including oligopeptides,²⁻⁴ these methods are subject to severe size limitations. An ab initio calculation of even the smallest naturally occurring protein is well beyond the range of modern computers and programming techniques. Pentamers are the largest polypeptide units that have been studied so far by quantum mechanical techniques.^{3,4}

More approximate approaches⁵⁻²⁰ have therefore been devised to obtain the total energy of polypeptides. Most of these use simple expressions for the potential energy in which the parameters are evaluated empirically for each term that is thought to be physically significant (e.g., electrostatic terms, bond stretching terms). These partitioning methods can be applied to very large systems, since the energy of any conformation is computed in a fraction of the time required for an analogous quantum mechanical calculation. However, such partitioning is rather arbitrary, as are the mathematical forms chosen for the potential functions and the values of the empirical parameters.

We report here an alternate method of energy partitioning in which all contributions are evaluated quantum mechanically.²¹ This treatment also employs empirical parameters, but only in identifying those high-energy conformations in which certain residues are in close proximity.

II. Methodology

Previous quantum mechanical studies of polypeptides indicate that the total energy of certain conformations can be expressed approximately as the sum of pairwise interactions between residues. Using ab initio and approximate ab initio methods, respectively, Shipman and Christoffersen³ and Kleier and Lipscomb⁴ examined oligomers of glycine ranging in size up to the pentamer level. Only regular helices were considered in which the pair of dihedral angles ϕ and Ψ about the C $^{\alpha}$ atom were identical for each residue. In such structures, the relative orientation of any two peptide units is dependent only on the values chosen for the dihedral angles ϕ and Ψ , and on the number of additional units that separate the units of interest along the polypeptide chain. The interaction energy between each pair of peptide units was assumed to be dependent only on their relative orientation. Numbering peptide units consecutively along the chain, the interaction energy, ΔE_m , of two peptide units, i and $(i + m + 1)$, in a regular helical n -peptide