can still be observed towards a preferential occupancy of the sites with the highest charge density.

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A Potential Energy Surface for the Addition of Benzyne to Ethylene

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A potential energy surface for the cycloaddition of benzyne to ethylene, calculated by the extended Hückel method, is presented. The least-motion $2_s + 2_s$ approach is forbidden, while the allowed $2_s + 2_a$ process is at high energy. The computed reaction path is shown in Figure 3. It has as one important feature a dead end valley in which the ethylene polarizes the benzyne and interacts in a typical carbonium ion manner with the electrophilic terminus of the polarized bond. We believe this valley will simulate an intermediate. The reaction terminates by a complex rotation and relaxation leading to benzocyclobutene. The calculated potential energy surface does not at this time appear completely consistent with the experimental facts concerning energetics and stereochemistry.

Rapid reactions of unstable intermediates are no guarantee that such processes are concerted. The most common reactions of *o*-benzyne are the Diels–Alder and "ene" type additions (1) and (2).[1] These are both

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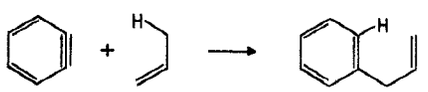

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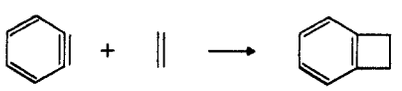


(3)

symmetry-allowed 4 + 2 cycloadditions,[2] anticipated to proceed in a stereospecific concerted manner. The stereochemical supporting evidence for concertedness has been obtained in both cases.[3-5] When neither reaction 1 nor 2 is available to a benzyne, but there is offered up to this reactive species a simple ethylene, there takes place a 2 + 2 cycloaddition resulting in benzocyclobutene (3).[1] This cycloaddition is highly exothermic. Though no kinetic information is available the reaction appears to take place readily at room temperature. We estimate an experimental upper limit of 15 kcal/mol for the activation energy to reaction 3.

The least motion $2_s + 2_s$ cycloaddition,[2a] in which the two reactants approach each other maintaining the C_{2v} geometry shown in Figure 1a, is a symmetry-forbidden process. This may easily be shown from a correlation diagram for the reaction or from our general arguments concerning concerted cycloadditions.[2] Despite the exothermicity of the process we would not expect a reaction following the forbidden path to proceed as readily as the actual reaction does.

$2_s + 2_a$ cycloadditions[2a] are symmetry-allowed and we turn to considering these. A benzyne adding in a 2_a manner is a stereoelectronic impossibility, since it would lead to a trans double bond or disruption of bonding in the benzene ring. A $2_s + 2_a$ cycloaddition, 2_s on the benzyne, 2_a on the ethylene, (approach geometry of Figure 1b) at first sight offers an attractive pathway. But a $2_s + 2_a$ cycloaddition appears to re-

(1) Benzyne chemistry is reviewed by Reinhard W. Hoffmann, "Dehydrobenzene and Cycloalkynes," Academic Press, New York, 1967, and T. L. Gilchrist and C. W. Rees, "Carbenes, Nitrenes, and Benzynes," Nelson, London, 1969.

(2) (a) For a definition of the 2_s, 2_a nomenclature see ref 2c, p 824; (b) R. Hoffmann and R. B. Woodward, *J. Amer. Chem. Soc.*, **87**, 2046 (1965); (c) R. B. Woodward and R. Hoffmann, *Angew. Chem.*, **81**, 797 (1965).

(3) R. W. Atkin and C. W. Rees, *Chem. Commun.*, 152 (1969).

(4) M. Jones, Jr., and R. H. Levin, *J. Amer. Chem. Soc.*, **91**, 6411 (1969).

(5) L. Friedman, private communication.

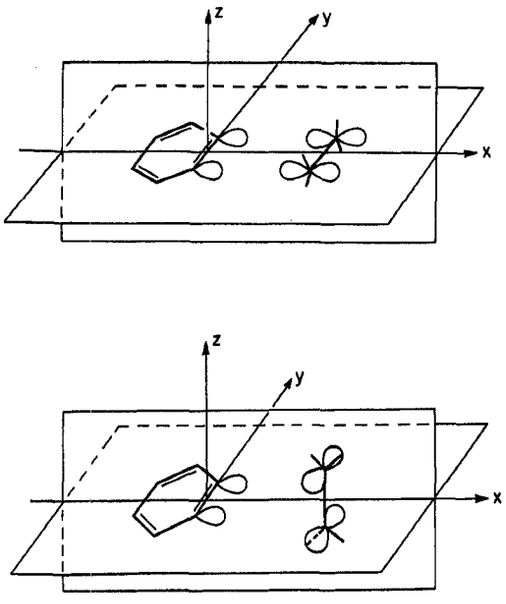


Figure 1. (a) Top. An approach geometry for the least motion $2_s + 2_s$ cycloaddition of benzyne to ethylene. (b) Bottom. One possible approach geometry for the $2_s + 2_a$ cycloaddition.

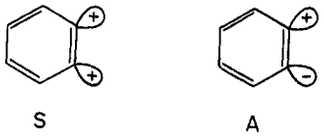
quire torsion in both components,[6] and such torsion is prohibitive for the benzyne which is constrained to a planar geometry.

We are left with postulating a nonconcerted process for this facile cycloaddition. Several groups have in fact found that the 2 + 2 cycloaddition of benzyne to cis or trans-substituted ethylenes is somewhat stereoselective but not stereospecific.[4,7-11] Whatever stereoselectivity is exhibited is not in the direction of a $2_s + 2_a$ addition.

In this paper we present an extended Hückel study of the potential surface for the addition of benzyne to ethylene. Our findings point up the complexities of many-dimensional potential surface explorations and reinforce the necessity of revising our naive view of nonconcerted reactions.

Benzyne

Before we begin our discussion of the potential energy surface we review our knowledge of the electronic structure of benzyne.[1,12-14] The two localized σ hybrids which one may imagine are left behind when two hydrogens are removed from benzene combine into a symmetric (S) and antisymmetric (A) pair. Any differentiation in energy between S and A is the consequence of interaction of the two hybrids with each other. The overlap of the hybrid lobes is relatively inefficient, and the splitting between S and A is consequently small.



S A

Configuration interaction mixes strongly the configurations $(S)^2$ and $(A)^2$. The resulting lowest singlet, of the form $c_1(S)^2 + c_2(A)^2$, $c_1 > c_2$, and the triplet of the configuration $(S)^1(A)^1$ compete for being the ground state of benzyne. The interaction between the hybrids appears to be just large enough to guarantee that the ground state of the *o*-benzyne is a singlet. The essential facts of the electronic structure of benzyne are the following. (1) The molecule possesses a singlet ground state with a low-lying triplet state an unknown energy above it. (2) There is in benzyne a high-lying occupied S level and a low-lying unoccupied A level. (3) The ground state singlet may be described as arising primarily from the configuration $(S)^2$, with a sizable admixture of $(A)^2$. (4) A weak third bond is a consequence of this description. We also anticipate good electron donor and electron acceptor properties from this easily polarizable third bond. In the introduction we mentioned that the least-motion cycloaddition of benzyne to ethylene is a symmetry forbidden process. This conclusion is based on the primacy of the configuration $(S)^2$ in the ground state wave function of benzyne.

Calculations

We carried out semiempirical molecular orbital calculations of the extended Hückel type.[15] Some seven degrees of freedom were allowed in our study. Three spherical coordinates D,θ,ϕ and three Euler angles[16] $\epsilon\phi$, $\epsilon\theta$, $\epsilon\psi$ were used to define the location and orientation of ethylene relative to benzyne. The origin of the spherical polar coordinate system coincided with the origin of the body-centered cartesian coordinates at the center of the benzyne triple bond (see Figure 2). The spherical polar vector D was directed to the origin of the body-centered coordinate system of ethylene (Figure 2).

The seventh degree of freedom studied was the "relaxation" of ethylene as it approaches the benzyne ring.

(6) Reference 2c p 828.

(7) I. Tabushi and R. Oda, *Tetrahedron Lett.*, 3743 (1968).

(8) L. Friedman, R. J. Osiewicz, and P. W. Rabideau, *ibid.*, 5735 (1968).

(9) M. Jones, Jr., and R. H. Levin, *ibid.*, 5593 (1968).

(10) H. H. Wasserman, A. J. Solodar, and L. S. Keller, *ibid.*, 5597 (1968).

(11) P. G. Gassman and H. P. Benecke, *ibid.*, 1089 (1969).

(12) T. Yonezawa, H. Knoishi, H. Kato, K. Morokuma, and K. Fukui, *Kogyo Kagaku Zasshi*, **69**, 869 (1966); T. Yonezawa, H. Knoishi, and H. Kato, *Bull. Chem. Soc. Jap.*, **41**, 1031 (1968); T. Yonezawa, H. Knoishi, and H. Kato, *ibid.*, **42**, 933 (1969).

(13) R. W. Atkin and T. A. Claxton, *Trans. Faraday Soc.*, **66**, 257 (1970).

(14) R. Hoffmann, A. Imamura, and W. J. Hehre, *J. Amer. Chem. Soc.*, **90**, 1499 (1968); M. D. Gheorghiu and R. Hoffmann, *Rev. Roum. Chim.*, **14**, 947 (1969).

(15) R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963); R. Hoffmann and W. N. Lipscomb, *ibid.*, **36**, 2179, 3489 (1962); R. Hoffmann and W. N. Lipscomb, *ibid.*, **37**, 2872 (1962). The hydrogen 1s exponent was 1.3.

(16) See H. Goldstein "Classical Mechanics," Addison-Wesley, New York, N. Y., 1950, p 107 for definition and sign convention of Euler angles.

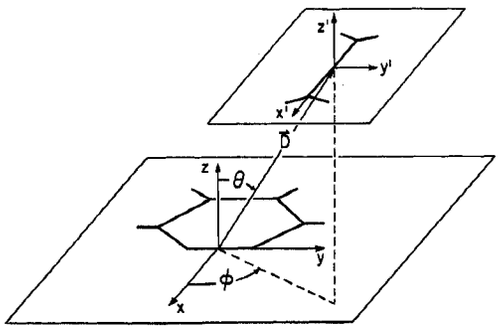


Figure 2. The coordinate system for benzyne and ethylene. Spherical coordinates $D(=r)$, θ, and ϕ locate the origin of the ethylene body-centered cartesian system with respect to the origin of the benzyne body-centered axes.

At large distances the molecular geometry of ethylene should remain unperturbed. As the molecule approaches benzyne we would anticipate the ethylene carbon–carbon bond to lengthen and the CH_2 groups to become pyramidal, culminating in a benzocyclobutene fragment geometry. We initially studied three stages of relaxation: "planar" (P), "partially relaxed" (PR), "relaxed" (R). Our results then forced us further to consider a fourth geometry "planar-partially relaxed" (PPR) in which the degree of relaxation differed at each carbon. The geometrical parameters for these four ethylenes are listed in Table I.

Table I: Geometrical Parameters of Various Stages of Relaxation of Ethylene

Relaxation state	C–C, Å	Angles HCH, deg	Pyramidality,[a] deg
Planar (P)	1.34	120, 120	0, 0
Planar-Partially Relaxed (PPR)	1.44	120, 115	0, 22.5
Partially Relaxed (PR)	1.44	115, 115	22.5, 22.5
Relaxed (R)	1.54	110, 110	45, 45

[a] Acute dihedral angle between the HCH plane and the body-centered $x'y'$ plane.

Benzyne was maintained as an idealized regular hexagon with all C–C, 1.40 Å; all C–H, 1.10 Å; all HCC and CCC angles, 120°. The C–H distance in ethylene was also maintained at 1.10 Å.

No attempt has been made to map the entire potential energy surface for the benzyne and ethylene system. Rather, the aim of this work has been to determine the reaction path and its vicinity. In our exploration of this path we were aided by an automatic minimum seeking program which utilized a procedure due to Rosenbrock[17] for finding those values of θ, ϕ, $\epsilon\phi$, $\epsilon\theta$, $\epsilon\psi$ which for a given D gave the lowest energy.

We present our computed reaction path in Figure 3—a sequence of snapshots of the two molecules at various separations.

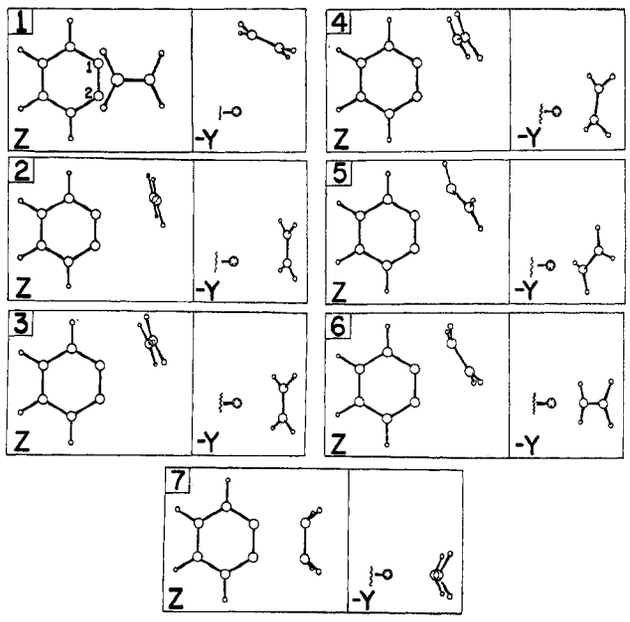


Figure 3. The computed reaction path presented as a series of snapshots. Each picture is presented as two views (not projections) from along the benzyne z and y axes. The snapshots are at D = 3.25, 3.00, 2.75, 2.50, 2.45, 2.28, and 2.25 Å in sequence. In the side view, only the carbons 1 and 2 of benzyne are shown, the rest of the molecule referred to by a wavy line. Pictures 1–3 are discussed in the "Distant Approach" section and pictures 4–7 are discussed in the "Terminating Approach" section. Picture 1 illustrates the "center" approach and picture 3 the "upright-side" approach. These illustrations were produced by a computer program due to C. K. Johnson, "ORTEP, a Fortran Thermal Ellipsoid Plot Program for Crystal Structure Illustrations," ORNL Report No. 3794, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965.

The Distant Approach

We first confirmed some of the qualitative conclusions reached in the introduction. Figure 4 shows how the energy varies along the least motion $2_s + 2_s$ approach for P and R ethylene. The degree of relaxation can influence the value of D at which level crossing occurs, but it cannot prevent that level crossing. The calculated activation energy for the forbidden reaction is approximately 1.7 eV.

In the $2_s + 2_a$ approach there takes place an effective torsion of 180° around the ethylene CC bond. Our study of the $2_s + 2_a$ approach was restricted to three degrees of freedom consistent with the twofold symmetry axis shown in Figure 1b: D, a torsional angle around the CC bond of ethylene, α, and a twist angle around the twofold axis, β. All geometries considered were even less stable than those in the $2_s + 2_s$ approach. Thus although the level crossing is avoided by joint rotation in α and β, there is not enough return in the bonding to make up for the energetic cost of twisting

(17) H. H. Rosenbrock and C. Storey, "Computational Techniques for Chemical Engineers," Pergamon Press, New York, N. Y., 1966.

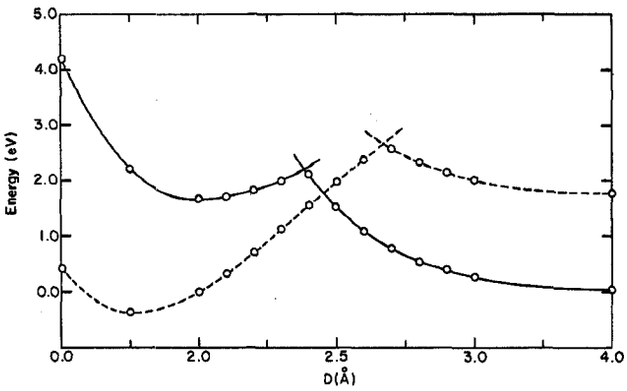


Figure 4. Computed potential energy curves for the least-motion approach of ethylene to benzyne. The solid line is for a planar P ethylene, the dashed line for a fully relaxed R ethylene.

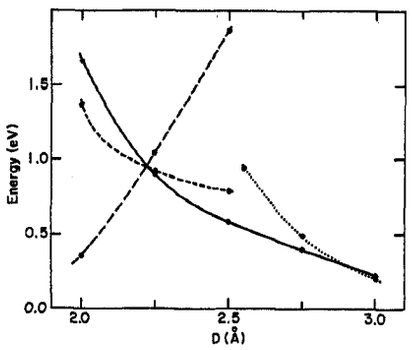


Figure 5. Potential energy *vs.* D for several ethylene approaches: ..... "center" valley; — "upright-side" approach of a planar ethylene; - - - - - - "upright-side" approach of a PR ethylene; — — $2_s + 2_s$ least motion approach for partially relaxed ethylene.

the ethylene. We attribute this to the previously mentioned fact that a $2_s + 2_a$ cycloaddition requires torsion in the 2_s as well as the 2_a component, and that this torsion, which was not allowed in our calculations, is unlikely in a benzyne.

The optimum orientation of an ethylene at large separation is not contained in the above two approaches. We searched the coordinate space at various D by varying independently the angles θ, ϕ, $\epsilon\phi$, $\epsilon\theta$, $\epsilon\psi$. A rough grid covered (at great cost) the entire range of these angles. The automatic minimization program allowed us then to home in on the true minima. In the region $D > 2.50$ Å we located two distinct potential energy valleys, corresponding to geometries which we will call "center" and "upright-side." These are illustrated in snapshots 1 and 3 of Figure 3. In the "center" geometry the ethylene is above the benzyne plane, tilted, but with its CC bond in the xz plane. The benzyne carbons are equivalent but the ethylene carbon atoms are not. In the "upright-side" geometry the ethylene orients itself off to one side, interacting more with one benzyne carbon than with the other. The ethylene carbons are now equivalent but those of the benzyne are not.

The optimized energies of the center and upright-side valleys are compared in Figure 5. At $D > 3.0$ Å the center minimum is at lower energy, while at $D < 3.0$ Å the upright-side minimum is at lower energy. We have confirmed that these are nevertheless independent valleys. The center valley persists until $D \cong 2.5$ Å, at which point a minimization procedure sends the molecule to the upright-side minimum. The upright-side minimum does not persist for $D > 3.2$ Å. The barrier between the two valleys was studied in some detail. It is very small at $D = 3.0$ Å; in fact the upright-side minimum at this point is slightly distorted (snapshot 2 of Figure 3) compared to its subsequent appearance (snapshot 3) in such a way as to take it partway toward the center minimum.

Figure 5 also contains a curve for an upright-side approach of a partially relaxed ethylene. At $D < 2.25$ Å this geometry is favored.

The Effective Intermediate

We are next faced with the problem of how the upright-side valley is converted to the benzocyclobutene. The upright-side valley, to whose extremely interesting electronic structure we will return in a moment, is clearly a *cul-de-sac*. Figure 5 indicates that partially relaxed or not the energy rises steeply as D is decreased. Also reproduced in Figure 5 is the energy of a partially relaxed ethylene $2_s + 2_s$ approach, taken from Figure 4. At $D < 2.25$ the PR approach, terminating in benzocyclobutene, is more stable than the PR "upright-side." Yet the latter continues to be a true local minimum, with respect to the angular parameters, at smaller D.

Molecules exploring this surface will probably usually proceed into the "upright-side" valley past $D = 2.25$ Å, even though such motion cannot lead to reaction. Reaction must occur by initiating in the region $2.3 \lesssim D \lesssim 2.6$ a rotatory motion by which the upright-side geometry is transformed into benzocyclobutene. It should be noted that the value of D at which rotation can take place is severely restricted. If we rotate at $D > 2.50$ Å then we find ourselves in-plane right at the point where the forbiddenness of the reaction is most strongly felt (see Figure 4). If we rotate at $D < 2.25$ Å we have already climbed within the upright-side valley to too high an energy.

The rotatory motion encounters initially a steeper portion of the potential surface than progress up the valley, but whereas the latter meets with increasingly stiffer resistance, the former leads to reaction. The situation is shown in a highly schematic two-dimensional contour map in Figure 6. Path A corresponds to the initially easy but ultimately nonproductive ascent into the valley of the upright-side geometry. Path B is the initially steep but ultimately productive

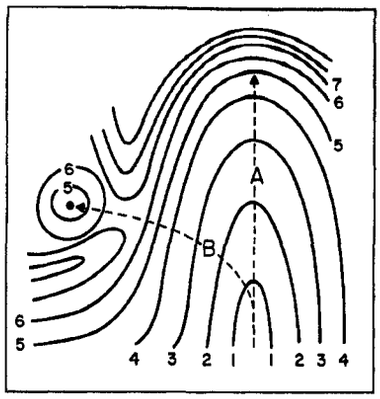


Figure 6. Schematic contour diagram. The vertical scale represents progress into the "upright-side" valley, while the horizontal scale models a rotation leading to benzocyclobutene. The contour values are arbitrary, indicating only the rise and fall of the energy.

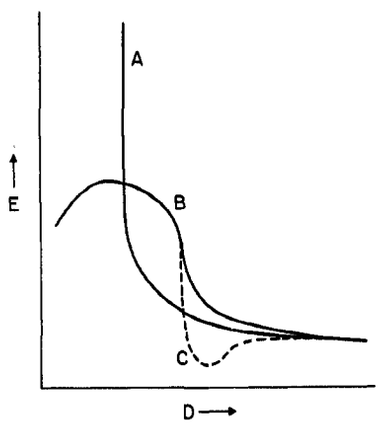


Figure 7. Schematic representation of the energy along paths A and B described in the "Effective Intermediate" section of the text. Curve C corresponds to the formation of a true intermediate.

optimum ascent. The energy variation along these paths is schematically drawn in Figure 7.

We think that typical molecular trajectories will unproductively explore the "dead-end" valley. The average molecule should then have a long residence time in the "upright-side" valley before it finds its way over to the product. Such long residence times would also result if the valley did not exist but instead there were a true local minimum, an intermediate, at a position close to where the optimum ascent out of the valley begins (curve C in Figure 7). It is clear that detailed trajectory calculations[18] are required to check our intuition on dynamic effects. *We think that a dead-end valley such as the one we discern here will be operationally indistinguishable from a true intermediate,* and as such constitutes another example of a *twixtyl*.[19]

The electronic structure of a typical "upright-side" oeometry becomes then of utmost interest as a model for such an intermediate. Figure 8 shows the important charges and overlap populations for such a model. It

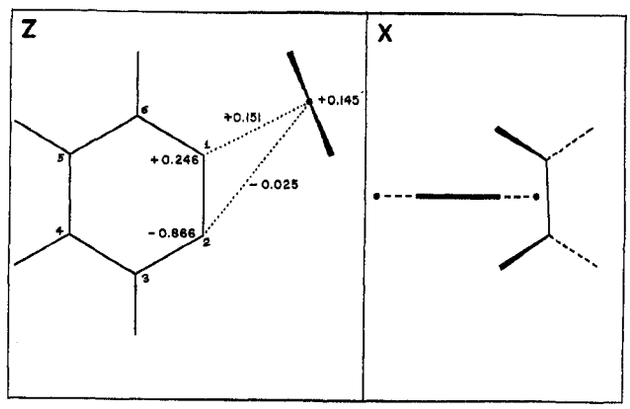
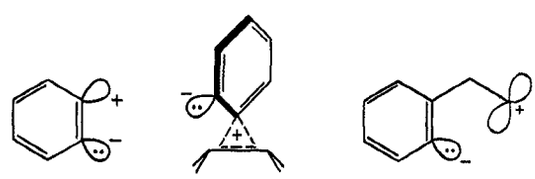


Figure 8. Two projections of a planar ethylene in "upright-side" valley at $D = 2.50$ Å. The significant overlap populations and charges are indicated. Note that one of the views is along the x axis, unlike the second views of Figures 3 and 9.

is not surprising to find some bonding to the near benzyne carbon, little bonding to the other. Note, however, the remarkable polarization of the benzyne, and the significant positive charge transfer to the ethylene. We may imagine that as the ethylene approaches it polarizes the benzyne third bond to a charge distribution corresponding to **4**, and that the polarized benzyne interacts in a typical electrophilic manner with ethylene



4 **5** **6**

to produce the species **5**. The electronic distribution of **5** is consistent with our computational results (Figure 8); this effective intermediate is rationally described as an internally compensated zwitterionic σ-phenonium ion. While it bears an obvious resemblance to other phenonium ions,[20] it carries its own counterion within itself.

In some of the experimental studies on the benzyne–ethylene cycloaddition the possibility of an intermediate closely related to **5**, namely the "classical" zwitterionic structure **6**, was considered.[10] The absence of major solvent effects on the observed stereochemical preferences was considered as partial evidence against the involvement of a species such as **6**.[11] We are not sure if the usual solvation arguments are applicable to a

(18) P. J. Kuntz, M. H. Mok, and J. C. Polanyi, *J. Chem. Phys.*, **50**, 4623 (1969); L. M. Raff and M. Karplus, *ibid.*, **44**, 1212 (1966); D. L. Bunker and N. C. Blais, *ibid.*, **41**, 2377 (1964), and related work by these and other research groups.

(19) R. Hoffmann, S. Swaminathan, B. G. Odell, and R. Gleiter, *J. Amer. Chem. Soc.*, **92**, 7091 (1970).

(20) D. J. Cram, *J. Amer. Chem. Soc.*, **86**, 3767 (1964); D. J. Cram in "Carbonium Ions," Vol. III, G. A. Olah and P. v. R. Schleyer, Ed., Wiley-Interscience, New York, N. Y., 1971.

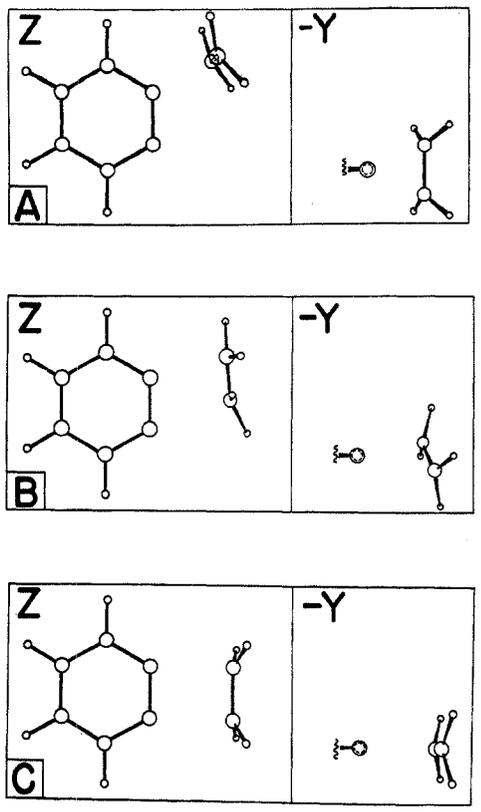


Figure 9. Views from along the z and y axes of benzyne of a transformation of PR ethylene from the "upright-side" valley to the product geometry. D is fixed at 2.25 Å while the motion is carried out with all five angular degrees of freedom changing by the same fractional amount in each step. A = beginning, B = middle point, C = end of rotation.

species such as **5**; since the positive and negative charges are held so close to each other, the species might appear neutral to an external solvent molecule.

The Terminating Approach

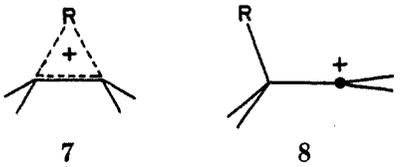
We turn to the final stages of the reaction, the transformation of the upright-side geometry into the product benzocyclobutene. Our first attempt involved a continuous transformation, treating all the angular parameters as varying in a correlated fashion, from the upright-side geometry to the benzocyclobutene structure for a partially relaxed ethylene at D = 2.25 Å. The beginning, midway, and end points of this motion are shown in projection in Figure 9. The potential energy along this path rose to a maximum of 1.7 eV above the separated molecules, a disappointingly large value in view of the potentially lower activation energy implied in Figure 5.

We found a lower activation energy path by two different procedures.[21] In the first process we began with planar ethylene in the upright-side valley at D = 2.50 Å at an energy of 0.58 eV (this and all subsequent unreferenced energies are relative to separated ethylene and benzyne). We rotated the ethylene by 90° around the line joining carbons 1 and 4 of benzyne (see Figure 8 for labeling convention). Since the perpendicular to the ethylene plane was very nearly collinear with the 1–4 axis, such a rotation keeps D approximately constant at 2.50 Å. The energy rises uniformly along with this motion, to a value of 0.90 eV when the ethylene carbons reach the benzyne plane. Optimization of the angular variables ϕ and $\epsilon\phi$ only, *i.e.*, restricting the ethylene CC bond to lie in the benzyne plane and the ethylene hydrogens symmetrically above and below that plane, led to a minor readjustment in geometry with a correspondingly small reduction in excitation to 0.87 eV.

In the next stage of the reaction the ethylene moves in to somewhat smaller D with the ethylene carbons in the benzyne plane but still off to the side. The energy climbs slowly along this stage of the approach. Since C(7) of ethylene is more strongly bonded than C(8) to benzyne carbon 1, we allowed partial relaxation at C(7), while keeping C(8) trigonal (see PPR geometry of Table I). The optimized P and PPR ethylenes are of nearly identical energy between D = 2.40 and 2.50 Å. At $D \cong$ 2.28 Å, which turns out to be the high energy point on our reaction path, the PPR ethylene (shown in snapshot 6 of Figure 3) is definitely more stable. The energy at this point is 1.19 eV above separated molecules.

The reaction terminates by an energetically downhill sequence. At $D \cong$ 2.25 Å the PPR geometry simultaneously partially relaxes the planar end and moves to a symmetric benzocyclobutene conformation. This spontaneously fully relaxes both ends as it descends in energy to a true benzocyclobutene (snapshot 7 of Figure 3).

The second pathway from the upright-side valley to the product derives from the observation that at D = 2.25 Å less than 0.1 eV is required to move the ethylene in the positive z-direction until the lower ethylene carbon is in the benzyne plane. This motion corresponds to converting a "nonclassical" geometry, **7**, to a "classical" conformation, **8**, of an ethyl cation. The calcu-



7 **8**

lated "softness" of the surface of this motion is consistent with the results of other calculations on model systems such as the ethyl cation.[22]

Moving the ethylene vertically up makes the ethylene carbon atoms nonequivalent. The lower in-plane car-

(21) Details for the energy surface search may be found in the Ph.D. Dissertation of D. M. Hayes, Cornell University, 1971.

(22) J. E. Williams, V. Buss, L. C. Allen, P. v. R. Schleyer, W. A. Lathan, W. J. Hehre, and J. A. Pople, *J. Amer. Chem. Soc.*, **92**, 2141 (1970); G. V. Pfeiffer and J. G. Jewett, *ibid.*, **92**, 2143 (1970); R. Sustmann, J. E. Williams, M. J. S. Dewar, L. C. Allen, and P. v. R. Schleyer, *ibid.*, **91**, 5350 (1969).

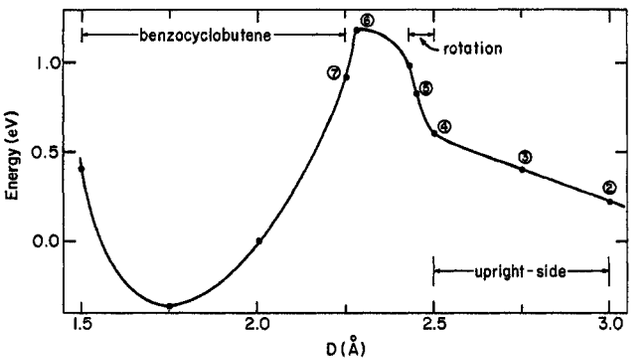


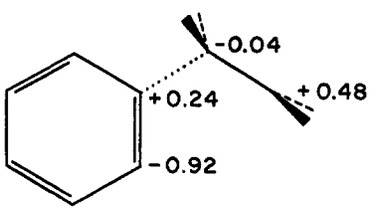
Figure 10. The calculated potential energy along the reaction path. The circled numbers correspond to the snapshots of Figure 3.

bon atom is expected to relax faster than the dangling upper carbon. Accordingly we changed the ethylene geometry to planar-partially relaxed and optimized its orientation at D = 2.50 Å. The resulting geometry, snapshot 4 of Figure 3, differs by only 0.02 eV from the symmetrical planar upright-side geometry. We now rotated the ethylene around the 1–4 axis of benzyne, until the carbon atoms of the ethylene were in the benzyne plane. The midway point of this rotation is snapshot 5 of Figure 3. At the termination of the rotation we optimized the geometrical parameters again, which resulted in a trivial displacement, and an excitation energy of 0.99 eV. It should be noted that, in the process of rotation into plane, D decreases from 2.50 to 2.43 Å.

At this point the alternative reaction path merges with the first one. The closure to benzocyclobutene proceeds as before, through an activation energy of 1.19 eV. The energy along the entire reaction path, previously illustrated in Figure 3, is shown in Figure 10.

It seems that the necessity to consider two branching pathways for the approach to the transition state is a consequence of our inadequate treatment of the degree of freedom of relaxation. Ideally, we should allow a continuous series of relaxations independently at each ethylene carbon. It may be that one clear reaction path would emerge in that case. But our computational resources do not allow us eight degrees of freedom, and the resolution of this problem remains for the future.

The transition state for the cycloaddition, approximated by snapshot 6 of Figure 3, possesses a highly unsymmetrical charge distribution shown below. The correspondence to a dipolar intermediate, **6**, is obvious,



and the same questions regarding the absence of solvent effects on this reaction[11] that were discussed above can be raised. It should be noted that the true charge imbalance in this geometry will be less than that shown above. First, extended Hückel calculations tend to exaggerate charge distributions. Second and more important, we are dealing with a formal diradical situation, meaning that we have two energy levels not far split in one-electron energy.[23] Let us call these levels HO and LU, for highest occupied and lowest unoccupied. HO is essentially a C_2 lone pair, while LU is heavily concentrated at C_8. The EH calculation considers only the configuration .... $(HO)^2$. To the extent that HO and LU are close in energy a more elaborate calculation will introduce configuration interaction and yield a ground state $c_1(HO)^2 + c_2(LU)^2$ which is much more balanced in the charge distribution.

We next studied the barriers to internal rotation in the ethylene fragment along the reaction path, in order to account for the observed nonstereospecificity of the cycloaddition. It is obvious that there should be a high barrier in the reactant ethylene and the product cyclobutene. The expectation that very low barriers would be found in PPR geometries near the transition state, where π-overlap between ethylene carbons is decreased, were however not met. The calculated barriers to twisting the terminal methylene group by 90° were certainly lower in the region between snapshots 4 and 7. However, they did not fall below 25 kcal/mol, much too high to account for the observed nonstereospecificity. The barrier can be lowered significantly by reoptimizing the angular parameters for a twisted ethylene fragment, and we believe that if greater flexibility is allowed to the ethylene the barrier will decrease further.

The Reaction Path

The benzyne–ethylene potential surface is a complicated one. We have identified three distinct potential energy valleys. These are (1) the distant centered approach, (2) the upright-side valley—a *cul-de-sac* simulating an intermediate, and (3) the product valley.

The reaction path for this cycloaddition is not easily defined. D—the distance between the center of the benzyne triple bond and the center of the ethylene—is a good reaction coordinate for large distances. Further in it is not at all clear that D serves as well. The minima of the potential surface are off to one side while D is basically a symmetrical coordinate. To move from the upright-side geometry to the transition state we were led to a rotation around the benzyne 1–4 axis —a motion which keeps D constant only for some special cases.

The lowest energy pass between reactants and prod-

(23) R. Hoffmann, *J. Amer. Chem. Soc.*, **90**, 1475 (1968); R. Hoffmann, G. D. Zeiss, and G. W. VanDine, *ibid.*, **90**, 1485 (1968); R. Hoffmann, A. Imamura, and W. J. Hehre, *ibid.*, **90**, 1499 (1968); R. Gleiter and R. Hoffmann, *ibid.*, **90**, 5457 (1968); *Tetrahedron*, **24**, 5899 (1968); *Angew. Chem.*, **81**, 225 (1969); R. Hoffmann, *Chem. Commun.*, 240 (1969).

ucts on this surface is fairly well defined. It occurs at the beginning of the product valley, corresponding to snapshot 6 of Figure 3. The calculated energy of this transition state is 1.19 eV or approximately 27 kcal/mol above separated products. This number is somewhat high, but in a reasonable range given the deficiencies of the computational method.

There is a wide range of reactive trajectories for this reaction. The one we think most closely approximates the true reaction path is given by the series of snapshots in Figure 3. The energy along this pathway was shown in Figure 10. An alternative trajectory which would encounter the same transition state but differ in the region of "rotation" is described in the previous section. Still another family of trajectories may be constructed by taking the transition state and pulling the ethylene off to infinity while maintaining the C(1)–C(7)–C(8) angle constant. If at the proper stages in this path relaxation is allowed for, such a motion would proceed along a path of uniformly decreasing energy on the large D side of the barrier. However these alternate trajectories, which could be followed by some specific molecule, do not constitute the reaction path, as classically defined. All the points along this trajectory, other than the transition state, would move to lower energy "upright-side" or "center" geometries at the same D. Nevertheless it is clear that a multiplicity of reactive paths with the same activation energy on this surface implies the importance of dynamic effects and reinforces the need for trajectory calculations.

It is important here to reiterate the deficiencies of our calculation. The computed activation energy is too high by approximately a factor of 2. The computed barrier to rotation of the ethylene along the reaction path is also too high to account for the lack of stereospecificity. While some of the disagreement may be due to lack of optimization of all degrees of freedom, we fear that the major source of discrepancy is to be traced to the inadequacies of the extended Hückel method. While there is some reason to believe, on the basis of our experience with many other systems, that the qualitative reaction path is reliably predicted, the results must be viewed with reservation until much better calculations are performed.

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