2 (and the corresponding nonalene), which manifests aromatic character.

A bis-Wittig reaction[7] was carried out between biphenyl-2,2′:6,6′-tetracarboxaldehyde[8] and 1,3-bis(triphenylphosphonium)propane dibromide in the presence of 1,5-diazabicyclo[4.3.0]non-5-ene affording 7*H*-dibenzo[*a,c*] cyclononene-1,13-dicarboxaldehyde (**3**,[9] 12% yield): mp 30 °C; *m/e* 274 (M, 19%); ν_{max}^{Nujol} 1700 cm^{-1} (C=O stretching); ^{1}H NMR δ ($CDCl_3$)[10] 2.67 (tt, 2 H, J_1 = 6.0, J_2 = 1.5 Hz, H_7, $H_{7'}$), 5.60 (td, 2 H, J_1 = 12.0, J_2 = 7.0 Hz, H_6, H_8), 6.16 (td, 2 H, J_1 = 12.0, J_2 = 1.5 Hz, H_5, H_9), 7.45 (m, 4 H, H_3, H_4, H_{10}, H_{11}), 7.85 (dd, 2 H, J_1 = 6.0, J_2 = 2.0 Hz, H_2, H_{12}), 9.56 ppm (s, 2 H, formyl). Under similar conditions, the consecutive Wittig reaction of **3** with the same phosphonium salt yielded 6,14-dihydrodibenzo[*gh,op*]nonalene (**4**, 7% yield)[9]: mp 112 °C, *m/e* 283 (M + 1), 282 (M, 70%), 281, 268, 254, 240 (100%), 202; $\lambda_{max}^{C_6H_{12}}$ 224 (ϵ 12 000), 260 (8000), 272 (sh) nm (6500); ^{1}H NMR δ ($CDCl_3$)[10] 2.76 (tt, 4 H, J_1 = 6.0, J_2 = 1.0 Hz, H_6, $H_{6'}$, H_{14}, $H_{14'}$), 5.53 (td, 4 H, J_1 = 12.0, J_2 = 6.0 Hz, H_5, H_7, H_{13}, H_{15}), 6.17 (td, 4 H, J_1 = 12.0, J_2 = 1.0 Hz, H_4, H_8, H_{12}, H_{16}), 6.85–7.20 ppm (m, 6 H aromatic). Irradiation at 2.76 ppm rendered the vinylic spectrum into a simple AB pattern. The NMR spectrum confirms a cis configuration for the double bonds (J = 12.0 Hz). It should be noted that the pattern of both the vinylic protons and of H_6, $H_{6'}$, H_{14}, and $H_{14'}$ are very similar to that of dibenzo[*a,c*]cyclononatetraene.[11] Even a tenfold excess of the phosphonium salt and base did not enable the direct synthesis of **4** from biphenyl-2,2′:6,6′-tetracarboxaldehyde.[7] Treatment of **4** with *n*-BuLi in THF-d_8 produced a deep red solution with the following ^{1}H NMR spectrum:[10] δ 2.92 (t, 2 H, J = 7.0 Hz, H_6, H_{14}), 4.62 (d, 4 H, J = 12 Hz, H_4, H_8, H_{12}, H_{16}), 5.86 (t, 4 H, J_1 = J_2 = 7.0 Hz, H_5, H_7, H_{13}, H_{15}), 6.80 (m, 2 H, aromatic), 7.08 ppm (m, 4 H, aromatic). We attribute this spectrum to a nonplanar, partially delocalized structure, **5**. A similar phenomenon has been observed upon deprotonation of dibenzo[*a,c*]cyclononatetraene.[11a] After some time at room temperature, the ^{1}H NMR spectrum of **5** disappeared; a new spectrum was concomitantly observed (the half life time of **5** is ca. 5 h). The following ^{1}H NMR spectrum was observed:[10] δ 6.35 (t, 2 H, J = 4.0 Hz, H_6, H_{14}), 6.67 (d, 4 H, J = 5.0 Hz, H_4, H_8, H_{12}, H_{16}), 7.01 (t, 4 H, J = 5.0 Hz, H_5, H_7, H_{13}, H_{15}), 7.20 (t, 2 H, J = 8.0 Hz, H_2, H_{10}), 8.35 ppm (d, 4 H, J = 8.0 Hz, H_1, H_3, H_9, H_{11}). This spectrum is assigned to the planar delocalized anion **1**. In spite of the formation of two negative charges, a downfield shift is observed in **1** relative to **5**. The chemical shift difference $\Delta\delta$**5**→**1** is 3.4, 2.0, and 1.25 ppm for H_6, H_{14}; H_5, H_7, H_{13}, H_{15}; and H_4, H_8, H_{12}, H_6, respectively. This downfield shift is attributed to the formation of a planar delocalized system. The absorption at 8.35 ppm is due to the proximity of H_4, H_8, H_{12}, and H_{16} of the planar nine-membered-ring system to the benzene moiety. The vicinal (ortho) coupling constants in **1** (J = 5.0 and 4.0 Hz) in contrast to the corresponding coupling constants of the partially delocalized dianion **5** (J = 12.0 and 6.0 Hz) indicates the formation of a planar aromatic dianion. Quenching of **1** or **5** produces a mixture of 4 and other allyl isomers.[12]

From all the above, it may be concluded that dibenzo[*gh,op*]nonalenide dianion (**1**) is a planar, delocalized diatropic dianion with a peripheral diamagnetic ring current. It is the first system to have been derived from the hitherto unknown nonalene skeleton.

Acknowledgment. We wish to acknowledge the financial support of The Israel Commission for Basic Research.

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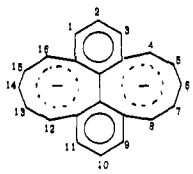
(12) Quenching of **1** or **5** with water resulted in the protonation of positions 4, 6, 8, 12, 14, and 16 (which correspond to positions with the highest charge densities according to HMO calculations). In the product mixture, **4** was identified in ~30% yield (NMR). The other isolated (PLC) quenching products (~45%) were identified as allyl isomers of **4** by catalytic hydrogenations and comparison with the hydrogenation product of authentic **4** (NMR, mass spectrum).



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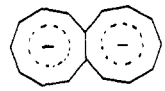

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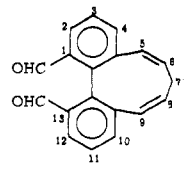

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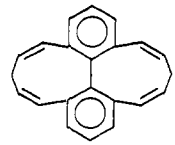

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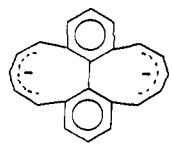

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Received December 29, 1976

Studies of Individual Methine Aromatic Carbon Sites of Proteins by Natural-Abundance Carbon-13 Nuclear Magnetic Resonance Spectroscopy at High Magnetic Field Strengths

Sir:

Natural-abundance ^{13}C Fourier transform NMR spectra of small globular proteins have yielded numerous narrow individual-carbon[1] resonances of nonprotonated aromatic carbons (Figure 1), even at magnetic field strengths as low as 14

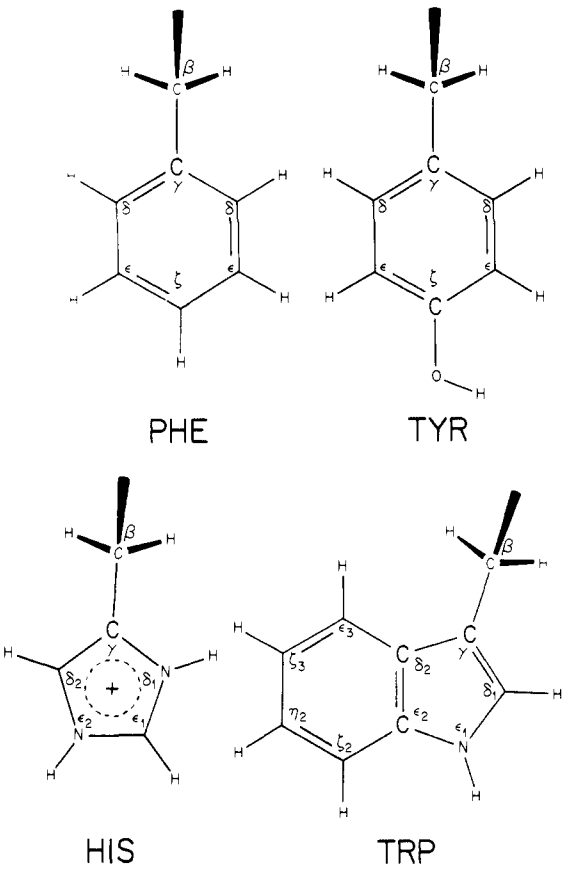

Figure 1. Structure of side chains of aromatic amino acid residues.

kG.[2-4] In contrast, the methine aromatic carbons of the same proteins (Figure 1) have yielded broad resonances (usually multiple-carbon bands) in natural-abundance ^{13}C NMR spectra at 14.2[2-7] and 23.5 kG.[8] The large difference between the line widths of methine and nonprotonated aromatic carbon resonances of native proteins at low magnetic field strengths results from the difference in the magnitude of the ^{13}C-^{1}H dipolar contributions to the spin–spin relaxation rates of the two types of carbons.[2] At high magnetic field strengths (such as 63 kG), chemical shift anisotropy (CSA) becomes the dominant relaxation mechanism for the nonprotonated aromatic carbons, but ^{13}C-^{1}H dipolar relaxation is still dominant for the methine aromatic carbons.[9] As a result, the difference between the line widths of the two types of resonances is considerably less at 63 kG than at 14 kG.[9]

In this report we show that the use of high magnetic field strengths (such as 63.4 kG) permits the observation of some resolved resonances of individual methine aromatic carbons of small native proteins. We present spectra of hen egg-white lysozyme, and specific assignments for the resonances of C^{δ} of each of the three tyrosine residues of this protein. These resonances yield upper and lower limits to the rates of rotation of the aromatic rings about the C^{β}–C^{γ} bonds.

In Figure 2B we show most of the aromatic region of the fully proton-decoupled natural-abundance ^{13}C NMR spectrum (at 63.4 kG) of hen egg-white lysozyme (15 mM protein in H_2O, pH 2.9, 32 °C).[10] Only the resonances of C^{ζ} of the three tyrosine residues (at 154.5, 156.5, and 156.6 ppm downfield from Me_4Si[3]) are outside the range of chemical shifts of Figure 2. The recycle time (interval between 90° radiofrequency excitation pulses) of 0.4 s used for Figure 2B is much shorter than the spin-lattice relaxation times (T_1) of the nonprotonated aromatic carbons (~1.5 s under the conditions of Figure 2[9]), but much longer than the T_1 values of the methine aromatic carbons (about 0.2 s[11]). Therefore, the integrated intensities of the nonprotonated carbon resonances should be much lower than those of the methine carbon resonances in Figure 2B, even though we observed no major differences between the nuclear Overhauser enhancements (NOE) of the two types of resonances.[11] Nevertheless, it is desirable to determine experimentally the positions and intensities of the nonprotonated carbon resonances in Figure 2B, because some of these resonances are expected to overlap with those of methine carbons (see below). Figure 2C shows a spectrum recorded under the same conditions as those used for Figure 2B, except that noise-modulated off-resonance proton decoupling[3,5,9] was used. Under the proton-decoupling conditions of Figure 2C,[10] the methine carbon resonances are "smeared out," while the nonprotonated carbon resonances are just as narrow as with full proton decoupling.[3,5,9] Note that the same recycle time was used for Figures 2B and 2C. Therefore, each of the narrow peaks of Figure 2C should have a counterpart of the same intensity in Figure 2B. The importance of the choice of recycle time is illustrated in Figure 2D, which was obtained under the same conditions as Figure 2C, but with a recycle time of 2 s instead of 0.4 s. As expected on the basis of reported T_1 values,[9] the signal-to-noise ratio (for the nonprotonated carbon resonances) is much higher in Figure 2D than in Figure 2C, even though fewer accumulations were used for Figure 2D.

In Figure 2B, peaks which arise from methine aromatic carbons (as determined from a comparison of Figures 2B and 2C) are designated by numbers with a prefix M. A few of these peaks contain contributions from nonprotonated carbon resonances (designated by numbers with a prefix N). The *intensities* of these contributions are given directly by the intensities of the narrow peaks in Figure 2C, while the *positions* of the nonprotonated carbon resonances are more clearly established from Figure 2D. Our results indicate that it is possible to set up instrumental conditions which favor the observation of methine aromatic carbon resonances (Figure 2B), and other conditions which permit the study of the nonprotonated carbons without severe interference from the methine aromatic carbon resonances (Figure 2D). It is noteworthy that the relatively short T_1 values of the methine aromatic carbon resonances permit the detection of these resonances in a much shorter accumulation time than is necessary for observing the nonprotonated carbon resonances.

Figure 2A shows typical chemical shifts of the aromatic carbons (except C^{ζ} of tyrosine residues) of nonterminal aromatic amino acid residues of small peptides in aqueous solution.[12-15] A comparison of Figure 2A (and the ^{13}C NMR spectrum of denatured lysozyme[6]) with Figure 2B indicates that folding of the protein into its native conformation produces significant chemical shift nonequivalence of many of the types of methine aromatic carbon resonances, a behavior analogous to that observed for the nonprotonated aromatic carbon resonances (Figure 2D).[3,5] For example, peaks M27, M28, M29, M30, and M31 of Figure 2B can be assigned (on the basis of their chemical shifts) to $C^{\zeta 2}$ of the six tryptophan residues. The intensities of these resonances suggest that peaks M27, M29, M30, and M31 are single-carbon resonances (peaks M30 and M31 contain contributions from the nonprotonated carbon resonances N22 and N24, respectively). Each of the other types of methine aromatic carbons of tryptophan residues also exhibits significant chemical shift variations caused by protein folding (Figure 2B). The six δ carbons of the three tyrosine residues yield three partly resolved resonances (peaks M2, M3, and M4 of Figure 2B. In contrast, it appears that the six ϵ carbons of the three tyrosine residues yield a single resonance (peak M26).

It should be possible to assign many of the methine carbon resonances to specific amino acid residues in the sequence by means of the same methods used for assigning the resonances of nonprotonated aromatic carbons of lysozyme.[16] Here we present a few specific assignments. Details will be given else-

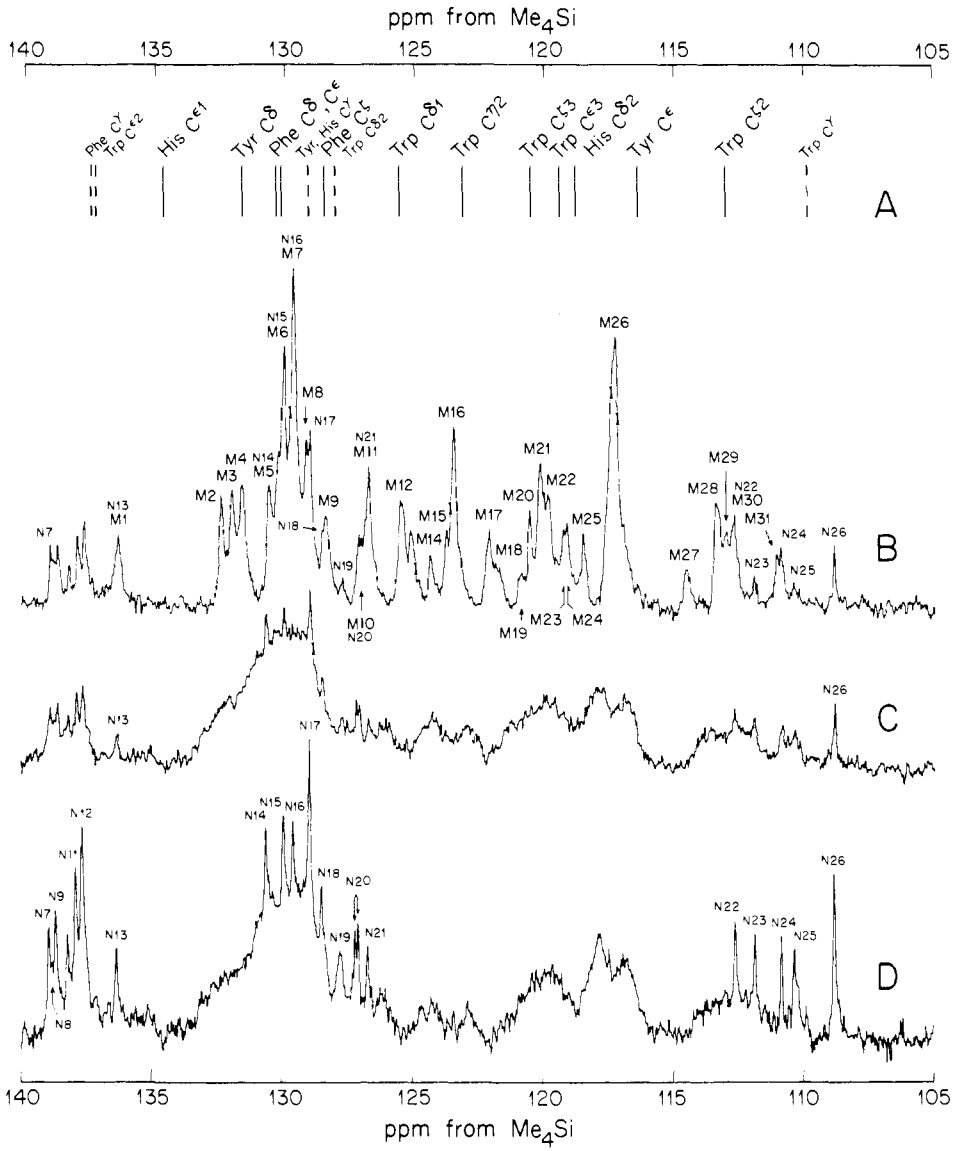

Figure 2. (A) Chemical shifts of methine carbons (solid lines) and nonprotonated carbons (dashed lines) of aromatic amino acid side chains of small peptides. The values for tyrosine (in the phenolic form) and histidine (in the imidazolium form) are those reported for these residues in angiotensin II.[12] The resonance of C^{ζ} of tyrosine (at 155.6 ppm[12]) is not shown. The values for phenylalanine and tryptophan are those for these residues in lysine-vasopressin[13] and luteinizing hormone-releasing hormone,[14] respectively. The assignments for $C^{\eta 2}$ and $C^{\zeta 3}$ of tryptophan are those of Bradbury and Norton.[15] (B) Region of aromatic carbons (except C^{ζ} of tyrosine residues) in the natural-abundance ^{13}C Fourier transform NMR spectrum of hen egg-white lysozyme (15 mM protein in H_2O, pH 2.9, 32 °C) at 67.9 MHz (63.4 kG), under conditions of full proton decoupling,[10] after 65 536 accumulations with a recycle time 0.4 s (7-h total time). The letters M and N designate methine and nonprotonated carbon resonances, respectively. The methine carbon resonances are numbered consecutively from left to right. The numbering system for the nonprotonated carbon resonances, which includes the resonances of C^{ζ} of tyrosines and arginines (not shown), is that of ref 2, 3, and 16. (C) As in B, except that the spectrum was recorded under conditions of noise-modulated off-resonance proton decoupling.[10] (D) As in C, but with a recycle time of 2 s and 32 768 accumulations (18-h total time).

where.[11] On the basis of the value and pH dependence of its chemical shift, we assign peak M1 to $C^{\epsilon 1}$ of the single histidine residue (His-15). At low pH (Figure 2B), peak M1 coincides with peak N13, assigned to $C^{\epsilon 2}$ of Trp-108.[16] The spectrum of a lysozyme sample preferentially iodinated at Tyr-23[16] (using iodine at pH 8.5[17]) indicates that peak M2 (Figure 2B) arises from C^{δ} of Tyr-23.[11] The broadening effect of the paramagnetic Gd^{3+} ion (bound in the vicinity of Glu-35 and Asp-52[18]) indicates that peak M3 arises from C^{δ} of Tyr-53.[11] By elimination, peak M4 is assigned to C^{δ} of Tyr-20.

Note that the chemical shifts of the two δ carbons of each tyrosine residue (see Figure 1) appear to be indistinguishable (Figure 2B), as is also the case for the reported ^1H NMR signals of the corresponding hydrogens (at 54 °C).[19] The ^1H NMR spectra have been interpreted as indicative of flipping of each phenolic ring between equivalent conformations, at rates exceeding 10^4 s^{-1} (at 54 °C).[19] We estimate that the contribution from chemical exchange to the line widths of peaks M2, M3, and M4 (at 32 °C, Figure 2B) is no greater than 5 Hz. If the difference in the chemical shifts of the exchanging sites is known, then we can compute the lower limit to the rate of flipping, with the use of the well-known equation for the exchange contribution to the line width of an exchange-averaged resonance.[20] If we assume that the chemical shifts of the two δ carbons of a tyrosine residue differ (in the absence of flipping) by more than 0.1 ppm (7 Hz), then the lower limit to the rate of flipping (at 32 °C) is 30 s^{-1}. An upper limit to the rate of flipping can be estimated from the T_1 and NOE values of peaks M2, M3, and M4. All three peaks have a T_1 of 0.20 ± 0.05 s and an NOE[21] of 1.3 ± 0.2.[11] These values are consistent with the rotational correlation time of lysozyme ($\sim 10^{-8}$ s under the sample conditions of Figure 2[22]) only if the rate of flipping of the phenolic rings is less than $\sim 10^8$ s^{-1}.[11]

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(1) We use the term "individual-carbon resonance" to designate a peak that arises either from a single carbon of a protein or from two or more equivalent carbons (such as the two δ carbons of a tyrosine or phenylalanine residue whose phenyl ring is undergoing fast internal rotation about the C^{β}-C^{γ} bond).
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Received March 22, 1977

On the Dichotomy between Cycloaddition Transition States Calculated by Semiempirical and ab Initio Techniques

Sir:

The timing of bonding changes in cycloaddition reactions has been the subject of many experimental investigations[1] and heated controversy.[2] The problem may be stated as follows: in a cycloaddition reaction where two new bonds are formed, are both bonds partially formed in the rate-limiting transition state, or is only one partially formed, the formation of the second occurring only after the rate-limiting transition state? Figure 1 shows the problem diagrammatically. All gradations between "bonding-concerted"[3] or "two-bond"[4] synchronous

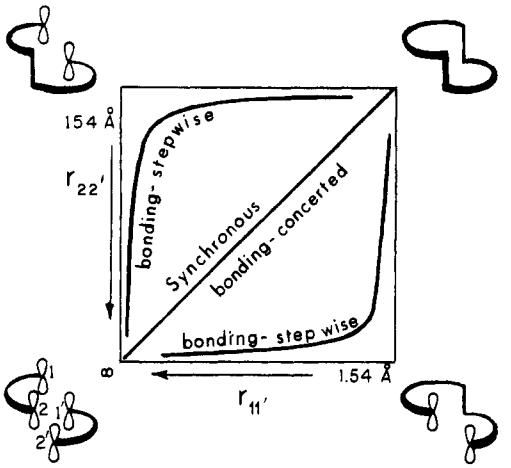

Figure 1. Bonding map for cycloadditions. The extreme pathways are labeled, but all variations are conceivable.

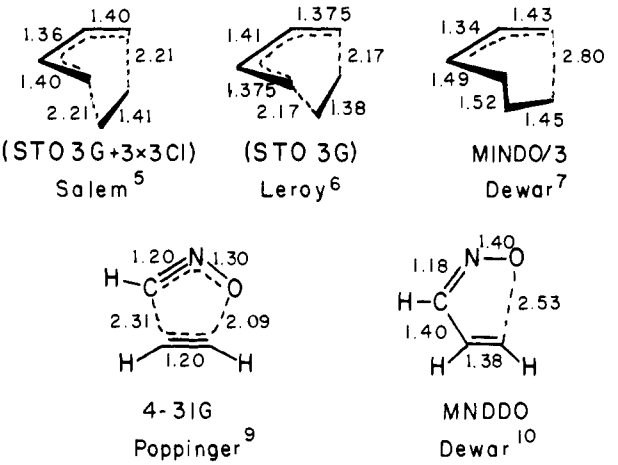

Figure 2. Cycloaddition transition-state geometries obtained from different calculations.

reaction pathways and "bonding-stepwise"[3] or "one-bond"[4] asynchronous pathways are possible. The question of the shape of the energy vs. reaction coordinate profile is, in principle, different, having to do with the absence ("energetically concerted")[3] or presence ("energetically stepwise")[3] of energy minima along the reaction coordinate.

Recently, detailed quantum mechanical calculations for two "classic" cycloadditions—a Diels–Alder reaction (butadiene + ethylene) and a 1,3-dipolar cycloaddition (fulminic acid + acetylene)—have been performed by several different techniques. These calculations predict distressingly dissimilar transition-state geometries (Figure 2). Two ab initio calculations have been published for the Diels–Alder transition state. The first used the STO-3G basis set with 3 × 3 configuration interaction (CI) to determine the lowest energy pathway, followed by calculations with the 4-31G basis and 3 × 3 CI for important geometries.[5] The second used a STO-3G geometry search, followed by recalculations of energies using a 7s,3p contracted basis set.[6] Although both concur on the synchroneity of σ bond formation in the transition state, the Leroy transition state is slightly "earlier" than the Salem.[6b] More disquieting is the comparison of these with the MINDO/3 transition state,[7] which is extremely unsymmetrical (biradicaloid) in nature. A point of agreement between the ab initio and MINDO/3 transition states is that no intermediates intervene between reactants and product.[8]

The dichotomy between ab initio and semiempirical calculations extends to calculations on the 1,3-dipolar cycloaddition of fulminic acid with acetylene. Figure 2 shows the transition