to the interatomic distances in the adduct. These results support Ingold's contention.

Secondary Interactions in the Transition State. For the three reactions studied with the strongly electron-withdrawing maleic anhydride as dienophile, the transition state was actually *smaller* than the volume of the corresponding adduct, even when solvent effects on the partial molal volumes of reactants and transition states are taken into consideration.

One might attempt to explain this by assuming that the diene and maleic anhydride, which are coplanar in the transition state, undergo a volume increase as new bonds are formed and the anhydride entity assumes its final position. A somewhat similar difference in position is found between *endo-* and *exo-*5-norbornene-2,3-dicarboxylic anhydride. The partial molal volumes for these compounds were measured with an injection dilatometer in two solvents of very different polarity. The results, given in Table III, show clearly that the

Figure 4. Schematic for the transition state for diene addition to maleic anhydride.

Table III. Partial Molal Volumes of *endo-* and *exo-*5-Norbornene-2,3-dicarboxylic Anhydride at Infinite Dilution

Adduct	Solvent, cc/mol	
	Nitromethane	Dichloromethane
endo	126.9 ± 0.4	123.7 ± 0.4
exo	127.4 ± 0.4	124.1 ± 0.4

volume difference between the two forms is far too small for this type of transition to account for the unusually small volumes of the maleic anhydride transition states.

Another possible explanation for these results is the possibility of secondary interactions in the transition complex. According to Hoffmann and Woodward,[12] the general rule for preferential formation of endo adducts can be explained by secondary π-electron interactions at nonbonding atoms. This concept may also explain the abnormally small volumes of the transition states for the maleic anhydride reactions. For example, for the maleic anhydride transition states as shown in Figure 4, bonds are being formed between carbon atoms 3 and 1' and between 4 and 4', while secondary interactions occur between 2 and 2' and between 5 and 3'. For the reaction of the acetylenic dienophile, in which the positions of nonbonding atoms do not allow secondary interactions to occur, the transition state is somewhat *larger* than the product, as expected. El'yanov, *et al.*,[29] have found that the volume of the transition state for the ortho-cis addition of *trans*-piperylene to methyl acrylate, which corresponds to endo addition, is smaller than the transition state for ortho-trans addition. This result can also be explained in terms of secondary π interactions in the endo transition state.

Investigations were carried out to ascertain whether the volume changes associated with π-complex for-

mation in solution are of a sufficient magnitude to account for the anomalously small volume of the maleic anhydride transition states—probably about 10–20 cc/mol smaller than expected. X-Ray diffraction studies of π molecular complexes in the solid state typically show a 10% decrease in intermolecular distance from the sum of the van der Waals radii.[30] Using the injection dilatometer, a measurement of the volume change accompanying formation of a π complex in dilute solution (0.05 M) was made for the tetracyanoethylene–durene complex in dichloromethane. An equilibrium constant, based on mole fraction, was determined for this system by Merrifield and Phillips.[31] The partial molal volumes for this system are shown in Table IV. As has been found for solid-state complexes,

Table IV. Partial Molal Volumes of Tetracyanoethylene, Durene, and Their π-Molecular Complex in Dilute Solution in Dichloromethane

Compd	Partial molal volume, cc/mol
Tetracyanoethylene	113.0 ± 0.5
Durene	159.1 ± 0.4
π complex	248 ± 5

the volume decrease for complex formation in solution is also about 10%. A somewhat smaller volume decrease accompanying π-electron interactions between nonbonding atoms would explain the anomalously small volumes of the transition states for the maleic anhydride reactions.

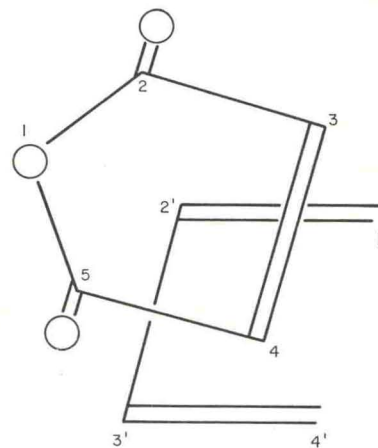(29) B. S. El'yanov, S. K. Shakhova, S. V. Vitt, and M. G. Gonikberg, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 565 (1969).

(30) D. S. Brown, S. C. Wallwork, and A. Wilson, *Acta Crystallogr.*, **17**, 168 (1964).

(31) R. E. Merrifield and W. D. Phillips, *J. Amer. Chem. Soc.*, **80**, 2778 (1958).