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Influence of Reactant Polarity on the Course of (4 + 2) Cycloadditions

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Abstract: An ab initio MO-theoretical study (RHF/3-21G* basis set and single point Becke3LYP/6-31G*//RHF/3-21G* calculations) on transition structures (TS) and intermediates in (4 + 2) cycloadditions of (*E*)-1-amino- and (*E*)-1-hydroxy-1,3-butadiene, of (*E,E*)-1,4-diamino- and (*E,E*)-1,4-dihydroxy-1,3-butadiene, and of 1,1-diamino- and 1,1-dihydroxy-1,3-butadiene to acrylonitrile, fumaronitrile, and 1,1-dicyanoethylene is reported. The amount of dissymmetry in bond formation increases with the capability of the reactants to stabilize a positive or negative charge. A main reason for the concomitant decrease in activation energy derives from polar interactions due to the transfer of charge from donor diene to acceptor dienophile. Zwitterions are located in the cycloaddition of 1,1-diamino- and 1,1-dihydroxy-1,3-butadiene to 1,1-dicyanoethylene if the solvent is included via the SCRF method. 1,1-Diamino- and 1,1-dihydroxy-1,3-butadiene form molecular complexes of van der Waals nature with 1,1-dicyanoethylene.

Introduction

Reactivity in Diels−Alder cycloadditions is best described by FMO theory, a model which is based on the presumption of a concerted pathway. While this mechanism seems to be realized for the majority of (4 + 2) cycloadditions there is an increasing number of examples which deviate from this rule by stepwise reaction via zwitterions or biradicals.[1] As in other types of reactions, e.g. nucleophilic aliphatic substitution, a continuous spectrum of mechanisms, ranging from concerted to stepwise via different intermediates, seems to be the best description of the actual situation.

Numerous ab initio MO-theoretical studies have been reported on Diels−Alder reactions. Many of them were concerned with the cycloaddition of butadiene to ethylene to elucidate the concerted or stepwise nature of this process.[2,3] The prototype, however, is not the typical case. A normal Diels−Alder reaction requires an electron-rich diene and an electron-deficient dienophile. It is the mechanism of these cycloadditions in which we are interested and for which some ab initio computational studies exist.[4−7] In this computational investigation we want to contribute to a better understanding of the influence of substituents on the mechanism of Diels−Alder reactions, in particular in cycloadditions of nucleophilic dienes to electrophilic dienophiles. As models for methoxy- and dimethylamino substituted dienes for which experimental results are available[8−11] we chose (*E*)-1-amino-1,3-butadiene (**1**), 1,1-diamino-1,3-butadiene (**3**), (*E,E*)-1,4-diamino-1,3-butadiene (**5**), and the corresponding hydroxy substituted dienes (**2**, **4**, and **6**). The study is particularly aimed at an understanding of the influence of a symmetrical vs a nonsymmetrical substitution pattern of diene and dienophile on the activation energy and the structure of the TS. Simultaneously, an analysis of regioselectivity and endo/exo selectivity is carried out where applicable.

Computational Procedures

The energies of ground states, transition structures (TS), intermediates, and products were determined by the GAUSSIAN 92 or the GAUSSIAN 94 program package.[12] In view of the size of the systems, structural optimizations were generally carried out with the 3-21G* basis set. Stationary points were fully characterized, e.g. TS, by an analysis of the Hessian matrix. The Becke3LYP density functional theory was applied in single point calculations with the 6-31G* basis set on RHF/3-21G* stationary points. One TS (**15**) was fully determined by Becke3LYP/3-21G* (100 h computation time on a CRAY-YMP). ZPVE were determined for all stationary points. ΔZPVE in Tables 1 and 2 refer to the difference of ZPVE for reactants and TS. E_a in Tables 1 and 2 are RHF/3-21G* values and values from single point Becke3LYP/6-31G*//RHF/3-21G* calculations including ΔZPVE. Simulation of the solvent was done with the SCRF option of GAUSSIAN 92.[13] Generally a dielectric constant (DK) of $\epsilon = 8.9$ was applied corresponding to the DK of dichloromethane.[14] In some cases $\epsilon = 2$ was studied in order to see the influence of different values of DK on the results.

Polar interactions and FMO stabilizations were calculated with the program PERVAL in either the MINDO/3 (polar interaction) or the

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Table 1. Data on Transition Structures (TS) of Cycloaddition of Amino-Substituted 1,3-Butadienes to Cyano-Substituted Dienophiles

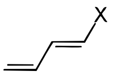
	$E_a{}^{a,b}$ (kcal mol^{-1})	$E_a{}^{a,d}$ + ΔZPVE (kcal mol^{-1})	μ [D]	HOMO$_{diene}$ − LUMO$_{dienophile}$ (kcal mol^{-1})	HOMO$_{dienophile}$ − LUMO$_{diene}$ (kcal mol^{-1})	Coulomb^{e} interaction (kcal mol^{-1})	charge^{f} flow (electron)	biradical^{g} character (%)	$r_1{}^h$ (Å)	$r_2{}^h$ (Å)
7	24.27 (26.60)^c	12.38 (13.89)^c	4.27 (5.58)^c	−13.6	−5.2	−3.87	0.243	7.9	2.015	2.483
8	26.05 (28.04)	13.76 (15.97)	4.24 (5.14)	−13.4	−5.0	−3.83	0.242	7.6	2.027	2.501
9	32.21 (33.03)	21.66 (22.27)	5.36 (6.82)	−11.2	−6.0	−0.84	0.165	2.9	2.183	2.183
10	32.66 (32.98)	22.09 (22.30)	5.76 (7.42)	−11.7	−5.9	−1.14	0.170	3.9	2.166	2.201
15a	11.82	1.13	5.10	−13.6	−2.4	−6.54	0.347	5.8	2.057	2.789
15b	−4.54	1.25	3.76						2.236	2.887
15a MC	−6.03	−4.70	3.11							
15b MC	−6.08	−3.42	2.30							
16	28.13	17.61	7.43	−19.4	−4.9	−2.08	0.273	3.2	2.256	2.109
19	22.47	11.20	4.65	−19.3	−3.5	−4.29	0.339	7.5	2.043	2.481
20	23.98	12.76	4.59	−18.8	−3.4	−3.27	0.326	6.9	2.082	2.436
23	29.15	15.79	3.96	−12.1	−5.1	−5.51	0.268	6.6	2.055	2.356
24	30.05	16.62	4.28	−12.3	−4.9	−6.02	0.269	6.3	2.064	2.367
27	22.95	11.22	3.39	−26.5	−3.3	−7.89	0.388	3.2	2.183	2.246
29	16.80	3.56	5.43	−19.9	−2.8	−12.05	0.424	6.1	2.024	2.661
31	5.00 (7.70)	−3.59 (−2.18)	4.67 (5.51)	−11.8	−1.1	−6.15	0.322	3.4	2.155	3.088
31 CA	−36.80 (−33.90)	−25.04 (−22.69)	4.23 (5.08)							
32	−8.34 (−5.77)	−5.07 (−3.76)	4.65 (6.13)							
33	−8.85 (−7.33)	−7.75 (−8.14)	5.09 (12.04)							
34	15.90 (−5.40)	2.76 (−16.50)	20.59 (19.39)							
35	13.40 (−56.80)	3.49 (−56.80)	27.14 (40.05)							
36	17.20	7.25	17.43							
42	35.20	23.80	7.95	−34.0	−5.2	−1.91	0.300	3.0	2.176	2.137
	$\epsilon = 2$	$\epsilon = 2$	$\epsilon = 2$							
34	5.08	−6.01	20.25							
35	−13.60	−12.79	33.58							

[a] Activation energies refer to the energy of the sp or sc conformation of the diene. [b] RHF/3-21G*. [c] Values in brackets: SCRF calculations (ϵ = 8.9). [d] Becke3LYP/6-31G*//RHF/3-21G*. [e] Increase of Coulombic interaction in TS due to charge transfer (MINDO/3−PERVAL). [f] Charge transfer from diene to dienophile in TS. [g] CAS(4,4)/3-21G* calculations. [h] Distances of reacting atoms, see formulas.

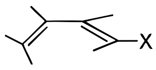
MNDO/PM3 parametrization.[15] The polar interactions were determined in a two-fold way. The structures of the TS were first separated into those of the individual reactants, then RHF/3-21G* calculations were done on these distorted structures and the Mulliken atomic charges of the individual reactants were used for the determination of the Coulombic interaction. In order to estimate the increase of the Coulombic interaction due to charge transfer in the TS, the Mulliken charges of the atoms in the TS were separated in two sets of the individual reactants and the interaction calculated again by PERVAL (MINDO/3). The FMO interactions were obtained similarly. MNDO/PM3 calculations of the reactants in their RHF/3-21G* TS were carried out and the orbital interactions in the TS were evaluated with PERVAL in the MNDO/PM3 parametrization. The orbital representations in some formulas derive from MNDO/PM3 calculations on the reactants in their transition state structure and refer always to HOMO$_{diene}$ and LUMO$_{dienophile}$ which are responsible for the strongest FMO interaction in these normal Diels−Alder reactions.[16] The amount of electron transfer in the TS was also determined by taking the RHF/3-21G* Mulliken charges in the TS, separating them in two sets of the reactants, summing them up individually, and taking their difference (dienophile − diene).

Ground States of Dienes and Dienophiles

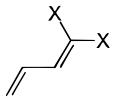
The results of the calculations on the ground states of the reactants are reported in the Supporting Information. The antiperiplanar conformations of the dienes (*E*-**1ap** and *E*-**2ap**) are 3.7 kcal mol^{-1} more stable than the second conformational minimum on the potential energy surface which does not correspond to a synperiplanar but to a synclinal (sc) arrangement where the two double bonds are twisted by 34° (*E*-**1sc**) and 39° (*E*-**2sc**). If the hydrogen atom at oxygen in *E*-**2sc** is rotated to the antiperiplanar position the structure becomes 2.6 kcal mol^{-1} less stable. Therefore, in this and all other examples the arrangement of the hydroxy group is fixed synperiplanar. Formulae **3**−**6** are representations of the ground state structures of the diamino- and dihydroxy-substituted 1,3-butadienes.



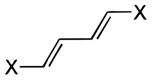
***E*-1ap** X = NH_2
***E*-2ap** X = OH



***E*-1sc** X = NH_2
***E*-2sc** X = OH



3 X = NH_2
4 X = OH



5 X = NH_2
6 X = OH

Transition Structures, Zwitterions, and Regioselectivity

Transition structures (TS) were located for four addition modes of acrylonitrile to (*E*)-1-amino-1,3-butadiene (Table 1). Of the four structures **7** and **8** correspond to "ortho" addition. Exo addition complex **7** is lowest in energy, being 1.4 kcal mol^{-1} more stable than **8**. The opposite regiochemistry, not observed for (*E*)-1-(dimethylamino)-1,3-butadiene, displays activation energies which are 9−10 kcal mol^{-1} higher than for "ortho" addition. At the unsubstituted ends of the reactants separations of 2.015 (**7**) and 2.027 Å (**8**) are determined for the reacting atoms while the substituted sides of diene and dienophile are ca. 0.5 Å farther apart. In **9** and **10**, however, more equal separations of ca. 2.2 Å are observed.

Why are TS **7** and **8** less symmetrical than **9** and **10**? In terms of FMO theory the structures of HOMO$_{diene}$−LUMO$_{dienophile}$ provide an explanation. The unsubstituted centers experience greater overlap of the π-orbitals and, therefore, stronger bonding. The non-synchronous TS leads to charge separation with partial

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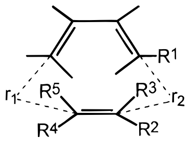
Table 2. Data on Transition Structures (TS) of Cycloaddition of Hydroxy-Substituted 1,3-Butadienes to Cyano-Substituted Dienophiles

	E_a[a,b] (kcal mol^{-1})	E_a[a,d] + ΔZPVE (kcal mol^{-1})	μ [D]	HOMO$_{diene}$ − LUMOdienophile (kcal mol^{-1})	HOMO$_{dienophile}$ − LUMOdiene (kcal mol^{-1})	Coulomb[e] interaction (kcal mol^{-1})	charge[f] flow (electron)	biradical[g] character (%)	r_1[h] (Å)	r_2[h] (Å)
11	30.50 (30.04)[c]	18.32	6.10 (7.41)[c]	−13.3	−6.6	−0.83	0.151	7.2	2.067	2.352
12	28.00 (29.45)	16.51	4.15 (5.15)	−13.6	−6.3	−1.84	0.164	6.6	2.084	2.348
13	32.10 (32.40)	21.31	5.50 (6.62)	−12.4	−7.0	−0.51	0.122	5.1	2.243	2.131
14	32.20 (34.32)	21.71	3.27 (4.09)	−13.0	−6.9	−0.67	0.126	4.7	2.226	2.148
17	20.33	7.50	6.99	−18.5	−4.4	−5.11	0.313	7.7	2.004	2.611
18	28.57	17.43	5.97	−18.8	−5.7	−2.03	0.236	6.3	2.329	2.061
21	28.79	17.33	3.84	−16.7	−4.7	−1.09	0.242	6.6	2.109	2.315
22	26.98	16.18	3.64	−16.7	−4.4	−1.56	0.247	5.6	2.158	2.269
25	33.29	20.90	7.14	−12.3	−7.2	−2.26	0.159	6.3	2.075	2.282
26	30.31	18.36	3.30	−12.7	−6.9	−3.55	0.173	5.9	2.090	2.280
28	29.05	17.50	4.62	−16.2	−4.8	−4.21	0.269	4.3	2.165	2.219
30	24.66	10.97	7.22	−18.6	−5.2	−7.80	0.318	7.3	1.994	2.486
37	12.94 (14.91)	0.27 (2.26)[c]	5.11 (6.15)	−16.8	−2.9	−10.56	0.370	5.8	2.025	2.861
38	−8.19 (−7.34)	−4.69 (−5.65)	7.67 (9.90)							
38 CA	−43.90 (−42.70)	−29.38 (−28.43)	5.79 (7.14)							
39	−5.61		1.79							
43	33.75	21.48	7.16	−23.2	−5.7	−4.28	0.293	5.5	2.308	2.076
	$\epsilon = 2$	$\epsilon = 2$	$\epsilon = 2$							
40	17.95 (5.73)	1.51 (−8.33)	20.75 (20.18)							
41	14.32 (−24.45)	2.63 (−31.68)	29.38 (37.63)							

[a] Activation energies refer to the energy of the sp or sc conformation of the diene. [b] RHF/3-21G*. [c] Values in brackets: SCRF calculations (ϵ = 8.9). [d] Becke3LYP/6-31G*//RHF/3-21G*. [e] Increase of Coulombic interaction in TS due to charge transfer (MINDO/3−PERVAL). [f] Charge transfer from diene to dienophile in TS. [g] CAS(4,4)/3-21G* calculations. [h] Distances of reacting atoms, see formulas.

charges at the substituted ends of the reactants. As explained above two calculations were carried out to probe this additional electrostatic stabilization of the TS. The difference of these interactions provides qualitative information about the amount of charge separation in the TS (Table 1). In **7**, the "ortho" exo addition mode, the Coulombic attraction increases from −3.1 to −7.0 kcal mol^{-1}, and in **8**, the "ortho" endo addition mode, a repulsion of +1.4 kcal mol^{-1} is converted to a net attraction of −2.4 kcal mol^{-1}. In both cases an increase of ca. −4 kcal mol^{-1} is found which must stem from a net flow of electrons from the donor diene to the acceptor olefin. Indeed, the flow of electronic charge, which was calculated for the reactants from the total electron densities in the TS **7** and **8**, is 0.24 electron, supporting the PERVAL analysis (Table 1). In **9** and **10**, the more symmetrical TS, a smaller gain in Coulombic stabilization goes along with a smaller flow of charge (transfer of 0.17 electron). The calculations thus confirm chemical intuition which led chemists to draw TS with partial charges and to use the feasibility of such structures as an argument for the observed regioselectivity and reactivity.



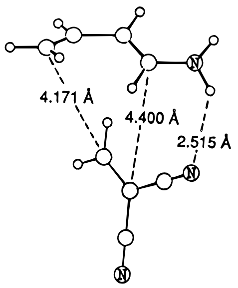
7 $R^1=NH_2$, $R^2=CN$, $R^3=R^4=R^5=H$
8 $R^1=NH_2$, $R^3=CN$, $R^2=R^4=R^5=H$
9 $R^1=NH_2$, $R^4=CN$, $R^2=R^3=R^5=H$
10 $R^1=NH_2$, $R^5=CN$, $R^2=R^3=R^4=H$
11 $R^1=OH$, $R^2=CN$, $R^3=R^4=R^5=H$
12 $R^1=OH$, $R^3=CN$, $R^2=R^4=R^5=H$
13 $R^1=OH$, $R^4=CN$, $R^2=R^3=R^5=H$
14 $R^1=OH$, $R^5=CN$, $R^2=R^3=R^4=H$

A similar analysis of the cycloaddition of (*E*)-1-hydroxy-1,3-butadiene to acrylonitrile (Table 2) showed that the "ortho" substitution products are favored over the "meta" products by 3.0 (**11** and **13**) and 5.2 (**12** and **14**) kcal mol^{-1}. The "ortho" endo product (**12**) is preferred which is in contrast to *E*-1-amino-1,3-butadiene where a slight exo selectivity had been noticed. The preference for "ortho" addition is less pronounced than in the case of the dieneamine *E*-**1**. The separation of the reacting atoms in **11** and **12** differs by ca. 0.3 Å which is less than the 0.5 Å in the case of *E*-**1**; thus, a slightly more synchronous bond formation is indicated. The TS for the non-expected "meta" orientation are more symmetrical, Δr being about 0.1 Å. The regiochemistry can be rationalized in terms of the structures of HOMO and LUMO of the dominant FMO interaction.[16] The amount of production of partial charges coincides with the non-synchronicity of bond formation. The amount of charge separation in **11**−**14** (Table 2) was determined in the same way as for **7**−**10**. A smaller flow of charge in these cycloadditions as compared to those of *E*-**1** to acrylonitrile produces smaller Coulombic interaction. This result goes along with chemical reasoning which suggests that a methoxy group is not as good at charge stabilizing as an amino group. It should be noticed that the amount of charge transfer here and in the previous case is greater in those TS which display bigger differences in the lengths of the forming bonds than if the TS is more symmetrical.

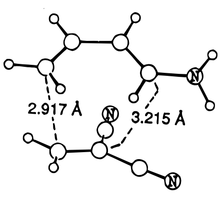
For TS **7**−**14** we determined the stabilizations from the FMO interactions by PM3-PERVAL according to the recipe given above. The stabilization energies (Tables 1 and 2) demonstrate that the reactivity in these cycloadditions is HOMO$_{diene}$−LUMO$_{dienophile}$ controlled, and the energy gain of this interaction is twice that of the second FMO interaction.

1,1-Dicyanoethylene serves as a model of a strong electrophilic and highly polarized dienophile. Compared with acrylonitrile it is expected that a second cyano group at the same C-atom will increase the capability of stabilizing a partial or full negative charge in the TS or a possible intermediate. The TS for "ortho" addition to *E*-**1** and *E*-**2** (**15** and **17** in Chart 1, Tables 1 and 2) are characterized by greater differences in the lengths of the forming bonds than in the case of the cycloaddition to acrylonitrile, Δ*r* being 0.6−0.7 Å. We used the addition of *E*-**1** to 1,1-dicyanoethylene for a comparison of the RHF/3-21G* (**15a**) and the Becke3LYP/3-21G* (**15b**) procedures. Thus, a full optimization of the TS was also carried out for Becke3LYP/3-21G*. The TS becomes slightly looser, and the difference in length of the forming bonds remains about the same. This result is pleasing as it suggests that our approach based on RHF/3-21G* geometries produces reliable results with respect to the synchronicity of bond formation.

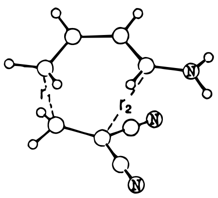
Chart 1



15a MC



15b MC



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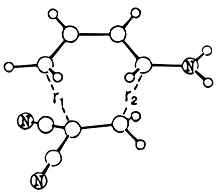

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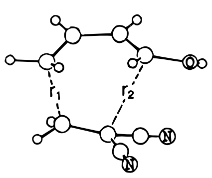

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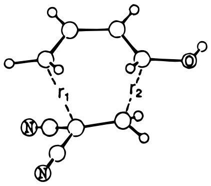


18

The activation energies of the cycloadditions were determined for different calculational procedures and are displayed in Figure 1. Including ZPVE a value of 14.3 kcal mol^{-1} (RHF/3-21G*) has to be compared with 1.1 (Becke3LYP/6-31G*//RHF/3-21G*) and 1.3 (Becke3LYP/6-31G*//Becke3LYP/3-21G*) kcal mol^{-1}, and with −2.3 kcal mol^{-1} (Becke3LYP/3-21G*). The decrease in E_a in correlated wave functions is expected, and the negative value indicates formation of a molecular complex (see Figure 1). It should be noted that RHF/3-21G* and Becke3LYP/3-21G* lead to molecular complexes of different structures where the result of the correlated wave function (**15b MC**) resembles more the TS of cycloaddition than **15a MC** (Chart 1). Relative to the van der Waals complexes all activation energies remain positive. Although E_a for the single point Becke3LYP/6-31G*//RHF/3-21G* calculation differs from that of the Becke3LYP/3-21G* optimization by 3.5 kcal mol^{-1}, the conclusions regarding the reactivity of 1,1-dicyanoethylene are not influenced by this numerical difference. The Becke3LYP/6-31G*//Becke3LYP/3-21G* value for E_a is only insignificantly different from the Becke3LYP/6-31G*//RHF/3-21G* evaluation.

If "meta" addition is assumed it is also possible to locate TS for the cycloadditions of *E*-**1** and *E*-**2** to 1,1-dicyanoethylene (**16** and **18** in Chart 1). These are more symmetrical, Δr being 0.15 and 0.27 Å. However, **16** and **18** are 16.5 (*E*-**1**) and 9.9 (*E*-**2**) kcal mol^{-1} higher in energy than the corresponding TS for "ortho" addition. A clear preference for "ortho" adduct formation is thus indicated.

Noteworthy conclusions can be drawn from the PM3-PERVAL analysis of the four TS. The FMO interactions show clearly a strong HOMO$_{\text{diene}}$−LUMO$_{\text{dienophile}}$ interaction in all cases, and a weak HOMO$_{\text{dienophile}}$−LUMO$_{\text{diene}}$ contribution which is expected on the basis of the strong electrophilic character of 1,1-dicyanoethylene. The greater discrimination between the two FMO interactions in TS **15**−**18** as compared to **7**−**10** is in line with the presumed reactivity of 1,1-dicyanoethylene which should be higher than that of acrylonitrile. The absolute values of the dominant FMO interaction in **17** and **18** are similar, but differ for **15** and **16** and, furthermore, favor the "meta" addition. Taking the dominant FMO interaction of the cycloaddition of *E*-**1** meta addition should take place, which is clearly not expected by chemical experience. The failure of the FMO model derives from the differences in the structures of **15** and **17** compared with **16** and **18** leading to better overlap and covalent bonding in the latter cases. A corrrect prediction of the expected regiochemistry can be made from an analysis of the structure of the relevant FMOs.

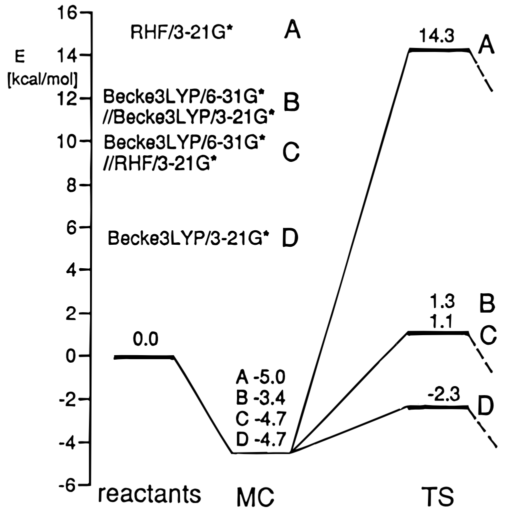
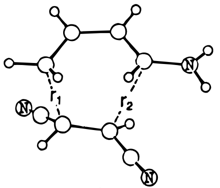
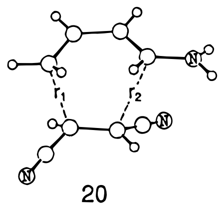


Figure 1. Reactions coordinate for the cycloaddition of (*E*)-1-amino-1,3-butadiene to 1,1-dicyanoethylene.

Chart 2



19



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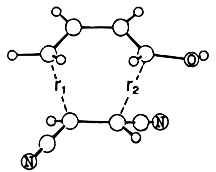

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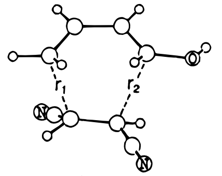
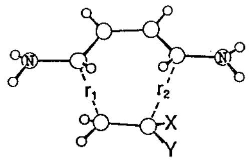


22

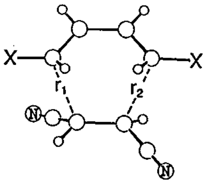
The overall preference for **15** and **17** can therefore not be due to covalent contributions, but must result from smaller non-covalent repulsions and stronger polar stabilizations. The gain in Coulombic attraction indicates charge flow from the donor to the acceptor molecule and parallels the amount of electron transfer (0.35 for **15** and 0.31 for **17)**. This transfer of electrons is smaller in the opposite regiochemistry, amounting to 0.27 (**16**) and 0.24 (**18**). TS **15** and **17** are indeed the structures where partial charges can be stabilized more easily.

Fumaronitrile can be arranged in two ways relative to the amino and hydroxy group of *E*-**1** and *E*-**2**:exo (**19** and **21**) or endo (**20** and **22)** (Chart 2) with respect to the cyano group next to the diene substituent. Compared to the TS of the cycloaddition of *E*-**1** and *E*-**2** to acrylonitrile the second cyano group in fumaronitrile, rendering the dienophile symmetrical, has little effect on the structures of the transition states. The

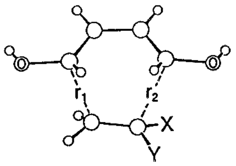
Chart 3



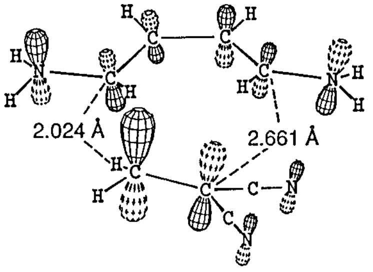
23 X=H, Y=CN
24 X=CN, Y=H



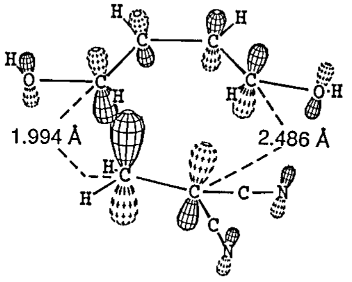
27 X=NH2
28 X=OH



25 X=H, Y=CN
26 X=CN, Y=H



29



30

new bond next to the substituent in the diene is longer. The reactants assume arrangements which can accommodate partial charges and should result in favorable Coulombic attraction. The values for these contributions confirm this presumption. The attraction increases by a factor of 2 in **19** and **20** if the charge distributions in the TS instead of those in the isolated molecules are used. This gain in stabilization is smaller for **21** and **22**. It should be noticed that the Coulombic attraction is greater in the exo TS **19** than in the endo TS **20**. For **21** and **22** this is just inverse. Parallel with this goes an exo-preference in the cycloaddition of *E*-**1** to fumaronitrile (1.6 kcal mol^{-1}) and an endo-selective addition of *E*-**2** (1.2 kcal mol^{-1}).

Fumaronitrile should display a reactivity comparable to 1,1-dicyanoethylene according to the FMO stabilization from the PM3-PERVAL analysis of **19**−**22** which, however, does not mirror the calulated activation energies (see Tables 1 and 2). As noted above the perturbational approach reaches the limit of its applicability when dissimilar structures are compared. In fact, the activation energies for the cycloaddition of *E*-**1** and *E*-**2** to fumaronitrile are only slightly lower than those for acrylonitrile and show the expected preference for *E*-**1** over *E*-**2** as diene. In terms of E_a 1,1-dicyanoethylene remains the most reactive dienophile in this series.

Although the dienes (*E*,*E*)-1,4-diamino- and (*E*,*E*)-1,4-dihydroxy-1,3-butadiene are symmetrically substituted molecules, the TS of cycloaddition to the non-symmetrical dienophile acrylonitrile have one of the forming bonds longer than the other: (**23**, **24**) and (**25**, **26**). The differences, however, are smaller than in those cases where both reactants are non-symmetrical. The amount of charge transfer in the transition structures is comparable to that in the cycloadditions to *E*-**1** and *E*-**2**. Similarly, the Coulombic attractions are comparable for both the mono- and disubstituted dienes. However, the FMO stabilizations calculated for the cycloadditions of 1,4-diamino- (**5**) and 1,4-dihydroxy-1,3-butadiene (**6**) are slightly *smaller* than in the cases of *E*-**1** and *E*-**2**. Compared with *E*-**1** and *E*-**2** a reduction in reactivity is, therefore, expected on the basis of the FMO interactions. The same conclusion is drawn from the activation energies which indicate also a higher reactivity of acrylonitrile toward the monosubstituted dienes than toward the 1,4-diamino- and 1,4-dihydroxy-1,3-butadiene. Exo addition of acrylonitrile is preferred for (*E*,*E*)-1,4-diamino-1,3-butadiene (0,8 kcal mol^{-1}) and endo addition should be favored for (*E*,*E*)-1,4-dihydroxy-1,3-butadiene (2.5 kcal mol^{-1}) paralleling the results for *E*-**1** and *E*-**2**.

The transition states **27** and **28** for cycloaddition of **5** and **6** to fumaronitrile are almost symmetrical as expected from the substitution pattern, a small distortion arises from the fact that one cyano group is located endo and the other exo. The balance of stabilizing and destabilizing forces is reached at a separation of ca. 2.2 Å of the reacting atoms. The FMO interactions reflect the strong donor and the high acceptor character of dienes and dienophile. In this respect the two amino groups are better π-donor substituents than the two hydroxy groups. The amount of charge flow and, simultaneously, the gain in Coulombic interaction are rather high and are connected to the strong donor and acceptor character of the reactants. The activation energies in these cycloadditions are comparable to those of the addition of fumaronitrile to the monosubstituted dienes. The activation energies indicate that fumaronitrile is more reactive than acrylonitrile toward the disubstituted dienes. The latter result is in agreement with qualitative observations for the cycloadditions of 1,4-bis(dimethylamino)-1,3-butadiene to the same dienophiles.[17,18]

Bond formation becomes less synchronous when 1,1-dicyanoethylene instead of fumaronitrile is added to **5** and **6** (**29** and **30** in Chart 3). The dominant HOMO-LUMO interaction, which can qualitatively be derived from the representations of these orbitals in **29** and **30**, suggests a rationalization for this phenomenon. The high contribution of the β-C-atom of 1,1-dicyanoethylene to its LUMO leads to a better overlap at this end of the diene and, therefore, to a stronger bonding. According to the analysis of the Mulliken charges, **29** and **30** show the highest amount of electron transfer from diene to dienophile in our series, 0.42 and 0.32 electrons. This is manifested also in the Coulombic stabilization of the TS, being 4.5 and 3.7 times higher than calculated for the Coulombic stabilization due to the Mulliken charge distribution of the isolated molecules in the TS arrangement. The activation energies for the cycloaddition of 1,1-dicyanoethylene to the 1,4-disubstituted dienes are ca. 3 kcal mol^{-1} higher than for the cycloaddition of the same dienophile to the monosubstituted dienes.

The analysis of the cycloadditions of 1,1-dicyanoethylene to 1,1-diamino-1,3-butadiene and 1,1-dihydroxy-1,3-butadiene was carried out because these reactants constitute prototypes of very non-symmetrical reaction partners and allow the elaboration of the consequences of this substitution pattern on the reaction

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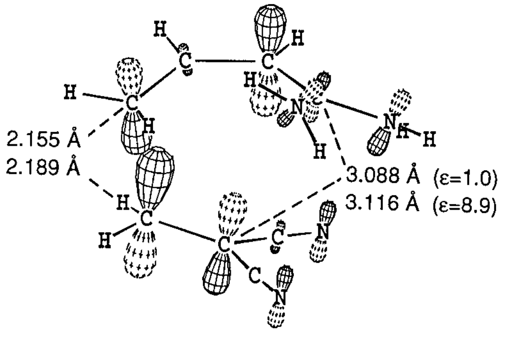
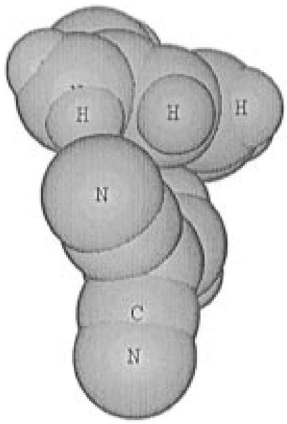
[17] Lücking, K.; Rese, M.; Sustmann, R. *Liebigs Ann.* **1995**, 1129−1138.

[18] Rese, M.; Dern, M.; Lücking, K.; Sustmann, R. *Liebigs Ann.* **1995**, 1139, 1152.

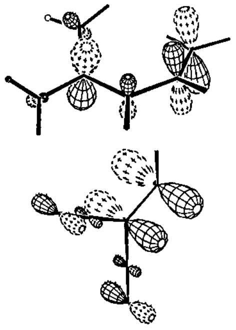
Chart 4



31



32a



32b

course particularly well. They also model experimental investigations which were carried out for bis(1,1-dimethylamino)-1,3-butadiene[8] and 1,1-dimethoxy-1,3-butadiene[11] with strong acceptor dienophiles like tetracyanoethylene. The strongly polar nature of the reactants suggests that solvent effects might become important. We, therefore, tried to mimic this situation by application of the SCRF procedure using a solvent with a dielectric constant of $\epsilon = 8.9$ (dichloromethane). Reference point for the calculation of the activation energies in these cases are the energies of the reactants calculated by the SCRF method in the same "solvent".

When the potential energy surface of the cycloaddition of 1,1-diamino-1,3-butadiene to 1,1-dicyanoethylene is searched for the TS of a concerted cycloaddition **31** is located which is characterized by strongly different distances of the reacting centers, Δr being 0.933 Å (Chart 4). A separation of more than 3.0 Å at one end of the complex and 2.15 Å at the other leads to appreciable covalent interaction only at the unsubstituted side. The structure constitutes, however, a real transition state and the cycloadduct is formed directly from this TS without involving an intermediate. The RHF/3-21G* activation energy for this process is 7.4 kcal mol^{-1}. If the concerted cycloaddition is modeled in solution the TS changes slightly and E_a increases by 2.5 kcal mol^{-1}(Figure 2). A drastic reduction of E_a to a negative value takes place when Becke3LYP/6-31G*//RHF/3-21G* single point calculations are carried out in the gas phase and in solution. E_a in solution is slightly less negative than the gas phase value. Because of the negative value of E_a we presumed the formation of a molecular complex. Indeed, such a complex can be found, the structure of which is shown in **32**. 1,1-Dicyanoethylene is found below the diene and rotated about the CC double bond in such a way that π-interaction of the relevant orbitals should not be important (**32b**). The space filling representation **32a** underscores that the nature of this complex is of van der Waals type. The potential energy gain in complex formation is smaller in a dielectricum of $\epsilon = 8.9$. Although single-point calculations on the RHF/3-21G* structure are carried out which might not be stationary points for Becke3LYP/6-31G*//RHF/3-21G*, all procedures predict a small activation energy to reach the TS of cycloaddition. The situation is shown graphically on the left side of Figure 2. The reference point is the synclinal conformation of 1,1-diamino-1,3-butadiene and the ground state geometry of the dienophile. The complex formation energy obtained by RHF/3-21G* is -7.4 kcal mol^{-1}. Becke3LYP/6-31G*//RHF/3-21G* reduces this to -5.1 kcal mol^{-1}, and in the "solvent" the stabilization is reduced to -4.7 (RHF/3-21G*) and -3.8 kcal mol^{-1} (Becke3LYP/6-31G*//RHF/3-21G*). The structure of the molecular complex **32** has to be commented on. It can be seen that a nitrogen atom of one cyano group is rather close to a hydrogen atom of one amino group. Thus, it might be that N$-$H$\cdots$N hydrogen bonding causes this perpendicular arrangement of diene and dienophile. As will be seen below molecular complex formation may take place in different arrangements of the reactants. There seem be several minima in the potential surface at larger distances of diene and dienophile which correspond to different van der Waals complexes.

A second set of calculations was performed starting from the more stable antiperiplanar conformation of the diene. The approach of the reactants leads to the formation of a molecular complex (**33**) which passes on to a transition structure for zwitterion formation (**34**) and a zwitterion (**35**). The energy of the TS (Figure 2) is 10.4 kcal mol^{-1} above that of the concerted cycloaddition and the zwitterion is a minimum in the potential energy surface above the energy of the isolated molecules. Thus, under these conditions which resemble isolated molecules in the gas phase the concerted pathway should be favored. A Becke3LYP/6-31G*//RHF/3-21G* evaluation shows a reduction of E_a to 2.8 kcal mol^{-1} and an energy of the zwitterion which is 0.6 kcal mol^{-1} above the energy of the TS. This latter result must be an artefact of the single point calculation. With respect to the preference in mechanism the density functional calculation does not modify the result of the RHF/3-21G* evaluation: *Concerted cycloaddition is still favored*.

The SCRF procedure leads to a different picture. The molecular complex (**33**) is -6.7 and the TS (**34**) -4.6 kcal mol^{-1} below the energy of the reactants. More than 50 kcal mol^{-1} is the gain in energy when zwitterion **35** is generated. The distance between the reacting carbon atoms in **34** and **35** depends on the strength of the dielectricum. In **34** it is elongated from 1.89 Å ($\epsilon = 1$) over 2.12 Å ($\epsilon = 2$) to 2.45 Å ($\epsilon = 8.9$). Also the zwitterion **35** changes the bond length with the dielectric constant, however, in the opposite direction. Figure 2 shows that the zwitterion is formed with a small E_a of 2.1 kcal mol^{-1} (RHF/3-21G* $\epsilon = 8.9$). Becke3LYP/6-31G*//RHF/3-21G* ($\epsilon = 8.9$) **34** is -16.5 kcal mol^{-1} below the energy of the reactants. As this is more negative than the corresponding complex formation energy of -8.1 kcal mol^{-1}, we conclude that the zwitterion is generated without any activation in solution. Driving force for its formation must be the high solvation energy which leads to a reaction energy for zwitterion formation that is more negative than the reaction energy for cycloaddition. The dependence of the energetic situation on the magnitude of the solvent polarity can be recognized from a single-point Becke3LYP/6-31G*//RHF/3-21G* calculation with $\epsilon = 2$. As in the RHF/3-21G* ($\epsilon = 8.9$) evaluation a small

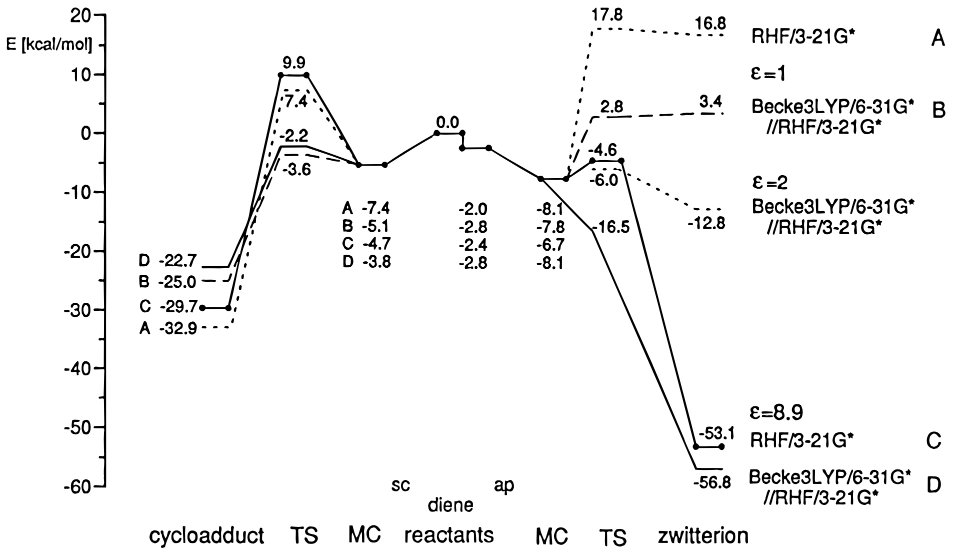


Figure 2. Reaction coordinate for the cycloaddition and zwitterion formation of 1,1-diamino-1,3-butadiene to 1,1-dicyanoethylene.

Chart 5

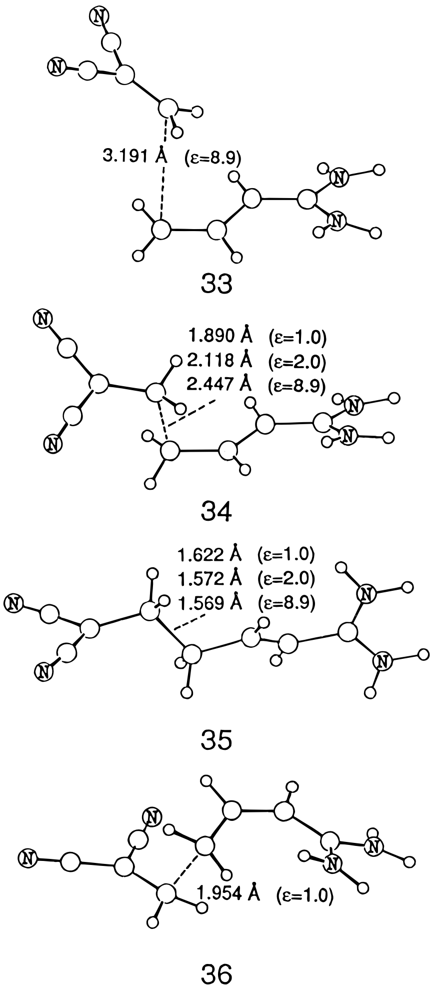
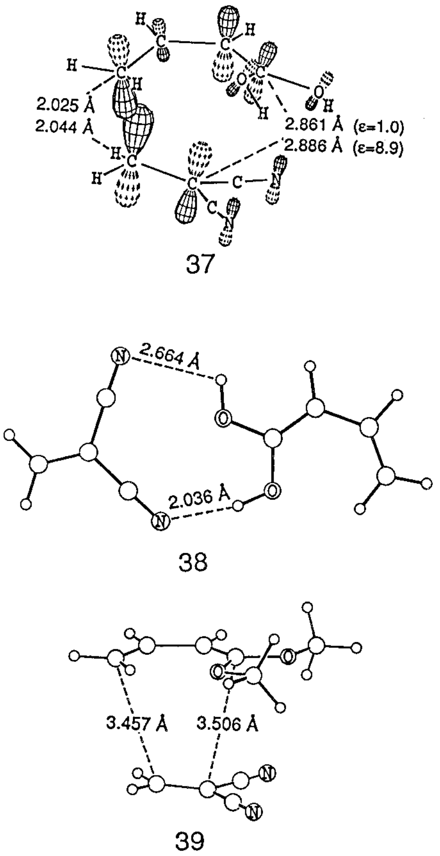


Chart 6



barrier seems to exist for zwitterion formation and its energy is −12.8 instead of −56.8 kcal mol^{-1} below the energy of the starting material (see Figure 2). Not only the antiperiplanar but also the synclinal (28°) conformation of 1,1-diamino-1,3-butadiene produces a TS for a zwitterion (ZI) in the gas phase when the dienophile is arranged as shown in **36**. On the way to the zwitterion it changes to the extended structure **34**.

The TS for the concerted cycloaddition of 1,1-diamino-1,3-butadiene to 1,1-dicyanoethylene is represented in **37**. A loose molecular complex **38** could be identified, its energy being −3.8 to −7.2 kcal mol^{-1} below the energy of the reactants depending on the type of calculation (see Table 2 and Figure 3). In **38** the nitrogen atoms of the cyano groups are positioned close to the hydroxy groups being thus in good hydrogen bonding distance. Indeed the N···H−O distances are 2.04 and 2.66 Å. This suggests that 1,1-dihydroxy-1,3-butadiene is not a good model for 1,1-dimethoxy-1,3-butadiene, at least not for the location of van der Waals complexes. Therefore, the hydroxy groups were replaced by methoxy and the search for a molecular complex was started again from the same geometry which led to **38**. A minimum in the potential energy surface was found (**39**) which resembled a widened TS, and the complex is −4.9 kcal mol^{-1} (RHF/3-21G*) below the energy of the reactants.

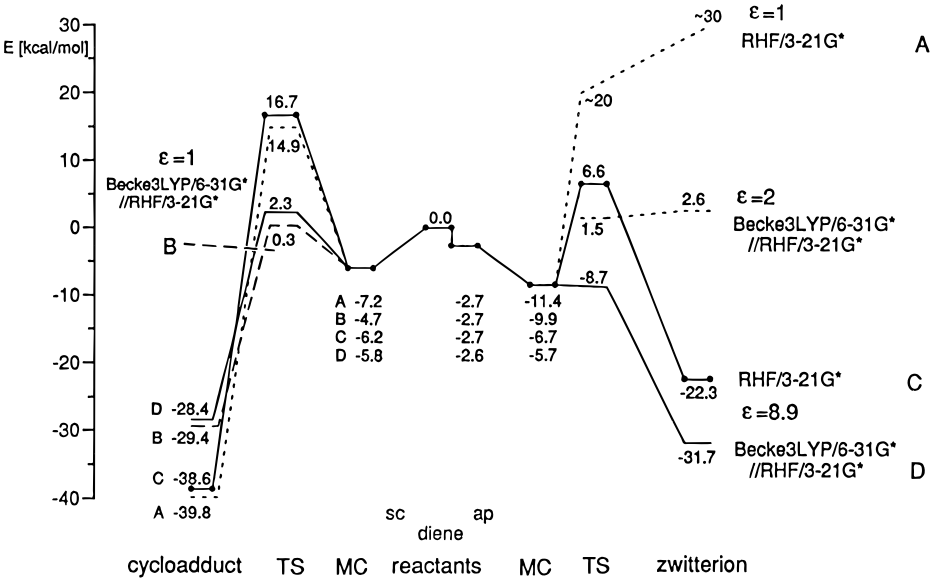


Figure 3. Reaction coordinate for the cycloaddition and zwitterion formation of 1,1-dihydroxy-1,3-butadiene to 1,1-dicyanoethylene.

This result made us curious whether still other minima in the potential energy surface might exist corresponding to van der Waals complexes. Indeed, two more such complexes were identified between 1,1-dimethoxy-1,3-butadiene and 1,1-dicyanoethylene being -7.5 and -7.2 kcal mol^{-1} more stable than the reactants. It can be safely assumed that there exist even more flat minima at these distances of the diene and dienophile.

TS **37** is characterized by highly unequal bond formation, 2.02 and 2.86 Å. It is a true TS which is 22.1 kcal mol^{-1} above **38**. It is characterized by a strong HOMO$_{\text{diene}}$−LUMO$_{\text{dienophile}}$ interaction and a weak LUMO$_{\text{diene}}$−HOMO$_{\text{dienophile}}$ interaction. The polarization in the HOMO$_{\text{diene}}$ and LUMO$_{\text{dienophile}}$ can be taken as part of the explanation for the nonsymmetrical structure of the TS. Furthermore, a drastic increase in polar stabilization is found for this structure. The analysis of the Mulliken charges indicates a transfer of 0.37 electron from diene to dienophile. The activation energy for cycloaddition is 14.9 kcal mol^{-1} which is reduced to 0.3 kcal mol^{-1} in the single point Becke3LYP/6-31G*//RHF/3-21G* calculation. The situation for different approximations is shown on the left side of Figure 3. Relative to the molecular complex **38** all activation energies remain positive, though very small for the single point Becke3LYP/6-31G*//RHF/3-21G* approximation.

Although a zwitterion could not be found starting with the synperiplanar conformation of the diene, there remains the possibility that such a species might be generated in an extended conformation. No TS for zwitterion formation could be determined by RHF/3-21G* without inclusion of solvation. Even a SCRF calculation for a solvent of low dielectric constant ($\epsilon = 2$) was unsuccessfull in this respect. At $\epsilon = 8.9$ a TS (**40**) and a zwitterion (**41**) are observed. The activation energy and the energy of formation of the zwitterion in the RHF/3-21G* approximation were obtained by single point calculations on the SCRF ($\epsilon = 8.9$) RHF/3-21G* geometry. If SCRF ($\epsilon = 8.9$) single point calculations are carried out with Becke3LYP/6-31G*//RHF/3-21G* the energies of both the TS and the zwitterion drop. The energy of the TS is even below that of the value of the molecular complex, obtained under the same conditions. This indicates that the zwitterion should be formed with negligible E_a.

The energies of formation of the zwitterion and the cycloadduct are comparable. In the case of 1,1-diamino-1,3-butadiene the zwitterion was 20−30 kcal mol^{-1} more stable than the cycloadduct. It seems as if this situation is mirrored in the experimental results for the cycloaddition of 1,1-bis(dimethylamino)-1,3-butadiene[8] and 1,1-dimethoxy-1,3-butadiene[11] to tetracyanoethylene. The dimethylamino-substituted diene forms a zwitterion at low temperature and shows no tendency for cycloadduct formation, while 1,1-dimethoxy-1,3-butadiene produces a zwitterion which cyclizes to the (4 + 2) adduct and can be trapped at low temperature.

In order to complete our analysis we searched for a TS of "meta" addition of 1,1-dicyanoethylene to 1,1-diamino- and 1,1-dihydroxy-1,3-butadiene. These combinations of dienes and dienophile do not lead to structures in which partial charges can be stabilized effectively. In view of our other results for this addition mode it is not surprising to find rather symmetrical TS (**42** and **43**) at distances of the reacting centers of 2.1−2.3 Å, typical for concerted Diels−Alder reactions. Activation energies of 23.8 and 21.5 kcal mol^{-1} prove that these reactions do not have a chance when compared with the "ortho" approach.

Reactivity and Biradical Character of TS

Dewar has been the proponent of biradical character of TS as an explanation of reactivity in Diels−Alder cycloadditions.[19] Biradical character can be calculated. One has, however, to be aware that the biradical character, as obtained for instance from CAS(4,4) calculations on the RHF/3-21G* transition structures, does not mean a structure with two unpaired electrons which behave like monoradicals. For the transition structures we determined values of their biradical character (Table 1 and 2). They range from 3 to ca. 8%, i.e. they remain in general rather small, and do not show a correlation with the reactivity in these systems.

Some trends can be recognized. In TS **7** and **8** the biradical character is 7.9 and 7.6%. In the regioisomeric TS **9** and **10** it is 2.9 and 3.9%. Indeed, **7** and **8** are the TS where chemical intuition suggests a stabilization of radical centers because the formation of one bond has progressed to higher extent than the other, and cyano and amino group are radical stabilizing substituents. A maximum of biradical character is reached when the difference in lengths of the new bonds in the TS is ca. 0.5 Å. It might be argued that the biradical character should be highest in the most dissymmetric TS **31** and **37**. This, however, is not true. In **31** it amounts to 3.0 and in **37** to 5.8%. Polar

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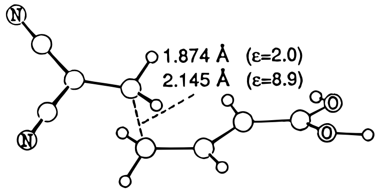
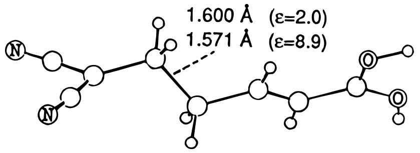
(19) Dewar, M. J. S.; Olivella, S.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1986**, *108*, 5771−5779.

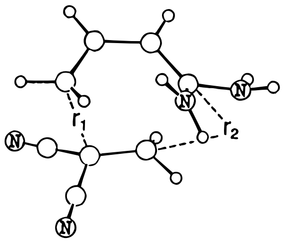
Chart 7



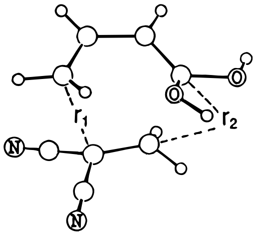
40



41



42



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rather than biradical configurations seem to be important for the stabilization of these transiton structures. The TS may be considered in terms of CI as superpositions of covalent, polar, and biradical configurations. Depending on the specific substitution pattern one or the other configuration will dominate the CI wave function. In our cases the polar contributions will be more important due to the charge stabilization capabilities of amino, hydroxy, and cyano groups.

Solvent Effects on Concerted (4 + 2) Cycloadditions

Solvent effects on the rates of concerted (4 + 2) cycloadditions are generally small.[1] In cases where zwitterion formation seems to be possible a dramatic change can be anticipated. The reactions of 1,1-bis(dimethylamino)- and 1,1-dimethoxy-1,3-butadiene with dimethyl dicyanofumarate are excellent examples.[10,11] SCRF calculations on the cycloadditions of 1,1-diamino- and 1,1-dihydroxy-1,3-butadiene to 1,1-dicyanoethylene showed that this method is capable of reproducing the expectations from experiment. We also carried out SCRF calculations for the cycloadditions of acrylonitrile to (*E*)-1-amino-1,3-butadiene and (*E*)-1-hydroxy-1,3-butadiene, using $\epsilon = 8.9$ (dichloromethane). A slightly higher activation energy (0.2−2.0 kcal mol^{-1}) but no change in mechanism is found. The TS for "meta" addition is influenced less than that for "ortho" addition. We conclude that in those cases where a stable zwitterion is not in sight, so that the concerted process is favored, solvation will not influence the activation energy noticeably. This is in line with experimental findings for concerted and zwitterionic Diels−Alder reactions.[1]

Discussion

An increasing number of donor substituents in the diene and of acceptor substituents in the dienophile enhances the rate of cycloaddition, i.e. lowers the activation energy. This general statement of the FMO model applies to the reactivity in normal Diels−Alder reactions.[16] Experimental experience, however, reveals that the picture is more complicated. Thus, it is found that (*E*,*E*)-1,4-dimethoxy-1,3-butadiene does not react faster than (*E*)-1-methoxy-1,3-butadiene in cycloadditions to tetracyanoethylene,[20] and that 1,1-disubstitution of the dienophile enhances the rate of cycloaddition more than 1,2-disubstitution.[21] Similar observations have been made for cycloadditions of dimethylamino substituted dienes to electrophilic dienophiles.[8−12] In this study we have calculated activation energies for the cycloaddition of donor substituted dienes to electrophilic dienophiles by ab initio theory and thus have a set of data to compare with experimental observations.

The trend in the activation energies which is found for the cycloaddition of (*E*)-1-amino- and (*E*)-1-hydroxy-1,3-butadiene to the series of cyano-substituted dienophiles is in line with experimental results for similar cycloadditions of these dienophiles to cyclopentadiene.[21] In particular the jump in reactivity from the symmetrically substituted fumaronitrile to 1,1-dicyanoethylene is well reproduced. What is the reason for the high reactivity of 1,1-dicyanoethylene in these cycloadditions? The FMO interactions cannot explain the trend. Here, fumaronitrile shows the highest $\mathrm{HOMO_{diene}}-\mathrm{LUMO_{dienophile}}$ stabilizations. For 1,1-dicyanoethylene and acrylonitrile the FMO stabilization are identical. The FMO interpretation fails which is not surprising because the structures of the TS which enter the calculation of the FMO stabilization are different. The calculated energies result from a dissection of the TS into distorted reactants, determination of their wave functions, and evaluation of the interaction in the transition state structure by PERVAL. The TS for cycloaddition of acrylonitrile and fumaronitrile display comparably short separations of the reacting atoms whereas the TS for cycloaddition of 1,1-dicyanoethylene shows one short (unsubstituted side of the reactants) and one long separation. Thus the overlap situation for covalent bonding is good for acrylonitrile and fumaronitrile but unfavorable for 1,1-dicyanoethylene. Nevertheless, the latter displays the lowest activation energy. The discrepancy between FMO theory and experimental result arises because we discuss only a single contribution to the activation energy and expect that this parallels the trend of the actual activation energies.

The transition state is reached when destabilizing and stabilizing contributions to the activation energy match exactly. Obviously, this state is reached in different ways for these dienophiles. In the TS the reactants no longer have their ground state structure. We calculated by PM3 the deformation energies for the RHF/3-21G* transition structures. These are +22.4 and 22.8 kcal mol^{-1} for **7** (acrylonitrile) and **19** (fumaronitrile), but only 16.4 kcal mol^{-1} for **15** (1,1-dicyanoethylene). Obviously a TS with less deformation of the ground-state structures is more favorable. Why do acrylonitrile and fumaronitrile not assume a TS similar to that of 1,1-dicyanoethylene? The answer to this question is that the former two dienophiles need a stronger deformation in the TS in order to use the gain in covalent interaction to counterbalance the destabilizing forces whereas the TS for cycloaddition of 1,1-dicyano-ethylene reaches this point of equilibrium with less covalent interaction but with a sizable Coulombic stabilization. The TS can thus be earlier on

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(20) Sauer, J.; Wiest, H.; Mielert, A. *Chem. Ber.* **1964**, *97*, 3183−3207.

(21) Rücker, C.; Lang, D.; Sauer, J.; Friege, H.; Sustmann, R. *Chem. Ber.* **1980**, *113*, 1663−1690.

the reaction coordinate! It is a consequence of the fact that two cyano groups at one C-atom stabilize partial negative charges better than only one such group. Qualitative support for this interpretation comes from the Coulombic stabilizations where the gain in stabilization is higher for 1,1-dicyanoethylene than for acrylonitrile and fumaronitrile as dienophiles. Less deformation energy of the reactants and at the same time an increased Coulombic interaction account for the high reactivity of the non-symmetrically substituted 1,1-dicyanoethylene compared with the symmetrical fumaronitrile.

Another interesting series of reactions can be compared: the cycloadditions of (*E*)-1-amino-1,3-butadiene, (*E*)-1,4-diamino-1,3-butadiene, and the corresponding hydroxy-substituted dienes to acrylonitrile. Although a second donor group in the diene should enhance its reactivity, the activation energy is 3.4 kcal mol^{-1} higher for the cycloaddition of (*E*,*E*)-1,4-diamino-1,3-butadiene and 1.8 kcal mol^{-1} higher for the cycloaddition of (*E*,*E*)-1,4-dihydroxy-1,3-butadiene than for the corresponding monosubstituted dienes. One contributing factor to this results is the smaller FMO interaction in the case of the 1,4-disubstituted dienes. The HOMO in the 1,4-disubstituted dienes is symmetrical, extends over six atoms, and has sizable contributions of the nitrogen and oxygen atoms. This leads to a dilution effect, i.e. the reacting C-atoms contribute less to the HOMO than in the monosubstitued dienes with the consequence of smaller covalent stabilization. The two other important factors for the smaller reactivity are the polarization of the HOMO of the monosubstituted dienes which leads to a favorable overlap situation at one side of the TS and the polar stabilization due to the charge transfer from diene to dienophile.

Conclusion

The activation energies (Becke3LYP/6-31G*//RHF/3-21G* + ZPVE) match closely the expected reactivity pattern in these cycloadditions. A satisfactory explanation for the different reactivity of symmetrical vs non-symmetrical substitution patterns can be provided within the perturbational framework. Particularly low activation energies are found when the reactants cannot only take advantage of covalent interactions but also of ionic stabilizations. If this possibility is given even a two-step mechanism becomes more favorable than a concerted one. The statement might be made that non-symmetrical TS are in general better than symmetrical ones and a one-stage concerted reaction path is only followed when no other possibility exists.

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Supporting Information Available: Tables of ab initio energies and dipole moments of ground states of dienes and dienophiles, ab initio energies and dipole moments on ground states of dienes and dienophiles by the SCRF method, ab initio energies of transition structures and cycloadducts for cycloaditions of amino-substituted and hydroxysubstituted 1,3-butadienes to cyano-substituted dienophiles and MINDO/3-PERVAL charge interaction in the RHF/3-21G* transition structures (4 pages). See any current masthead page for ordering and Internet access instructions.

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