Localized Bond (PVCILO) Calculations on the Cyanoethylene–Methyl Vinyl Ether Complexes

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Received December 14, 1990; Revised Manuscript Received December 3, 1991

ABSTRACT: The stabilization energies of donor–acceptor complexes (DA) possessing various geometries between methyl vinyl ether and cyanoethylenes such as acrylonitrile, maleonitrile, fumaronitrile, 1,1-dicyanoethylene, and tetracyanoethylene were calculated by the PVCILO method. The most stable geometry for each complex was obtained from the calculation, and the geometry was related to the spontaneous reactions of DA and stereoregularity of the products.

1. Introduction

Alkyl vinyl ethers (AVE) produce alternating copolymers when they copolymerize with fumaronitrile (FN) and maleonitrile (MN) via a radical copolymerization.[1] We suggested that the donor–acceptor complexes (DA) between AVE, which is an electron-donating molecule (D), and FN and MN, which are electron-accepting molecules (A), may participate in the copolymerization and that the stereochemistry of the copolymers might be affected by the geometry of the DA. Formation of DA is, however, not a sufficient condition for the stereoregularity. It also requires a specific opening of the double bonds that participate in the copolymerization.

In addition to FN and MN other cyanoethylenes such as acrylonitrile (AN),[2] 1,1-dicyanoethylene (DCNE),[3] and 1,1,2,2-tetracyanoethylene (TCNE)[4] are known to copolymerize or to form DA with various electron-donating molecules. In the cases of DCNE and TCNE, they actually lead to spontaneous formation of copolymers and cycloadducts, respectively, with D at low temperature. These spontaneous reactions are believed to occur by biradical or zwitterionic tetramethylene intermediates which are formed because of high polarities of the cyanoethylenes and AVE.[5-7] The dienophilic properties of cyanoethylenes which lead to formation of prereaction complexes have also been discussed by others.[8] The ability of cyanoethylenes to form DA with D is due to the presence of the electron-withdrawing cyano groups. Therefore, the ability of cyanoethylenes to form and the geometry of DA may depend on the number and the location of substituted cyano groups in the cyanoethylene. Consequently, we were interested in calculating the complexing ability and the geometry of DA formed from cyanoethylenes and methyl vinyl ether (MVE), a representative compound for AVE, by the perturbation and variational configuration interaction using localized orbitals (PVCILO) method.[9,10] This calculation gives stabilization energy (ΔE) and geometry of DA before DA actually forms any bonds or intermediates.

The PVCILO method is a modified PCILO (perturbation configuration interaction using localized orbitals)[11,12] method and is applied to predict the ability of DA formation and the most stable geometric structures of the DA. The PCILO method has been applied to calculate intermolecular interactions including DA,[13] hydrogen bonding,[14] and dimerization,[15] although the results did not show the transition states in the reactions.

The PVCILO method is not a molecular orbital based method. Instead, an antisymmetrized wave function is created from doubly occupied bonds between neighboring (bonded) hybrid orbitals, rather than doubly occupied molecular orbitals.[9-12] The energy is then developed through the Moller–Plesset–Rayleigh–Schrodinger theory. $E^0 + E^1$ is the energy of the bonded structure, whereas higher orders begin to correct for delocalization, charge transfer, dispersion, and so forth. This method seems particularly appropriate for explaining interacting subunits, each of which is well described by a simple valence bond structure, as it forms the corrections at higher order on the interaction energy itself.

The PVCILO method we used is based upon the CNDO/2 Hamiltonian, which at the Hartree–Fock (molecular orbital) level has a strong tendency to overbind systems. This disadvantage, however, is not apparent, even at fourth order in perturbation theory in the PCILO model which is based on this same Hamiltonian. For example, CNDO/2 Hartree–Fock calculations bind two benzene molecules by 250 kcal/mol. The same Hamiltonian applied within the fourth-order PVCILO function binds two benzenes in a T shape structure by 1.7 kcal/mol, a value in good agreement with those suggested through experiment.[16]

We have also examined the dimerization of ethylene and complexation between ethylene and MVE to validate the PVCILO calculation (Figure 1). ΔE for the dimerization of ethylene is −0.68 kcal/mol, and the distance between the ethylenes is 2.7 Å. The dimer is more stable when the double bonds are parallel to each other than when crossed over each other by 0.36 kcal/mol (Figure 1a). Ethylene and MVE also make a weak complex. The distance between ethylene and MVE is 2.7 Å, and ΔE is −0.96 kcal/mol. The parallel geometry is more stable than the crossed geometry (Figure 1b).

These results seem quite reasonable, so we examined the binding of cyanoethylenes to the MVE complex using the PVCILO method with some confidence.

2. Calculation

To make the calculation more treatable, we assumed that the geometry of the isolated donor and acceptor molecules did not change as they approached each other to form a complex. This assumption is based on an X-ray crystallographic study.[17] The geometry of DCNE was calculated using ab initio quantum mechanics (STO-3G bases set), and the geometric parameters of other molecules were obtained from the following references: *cis*- and

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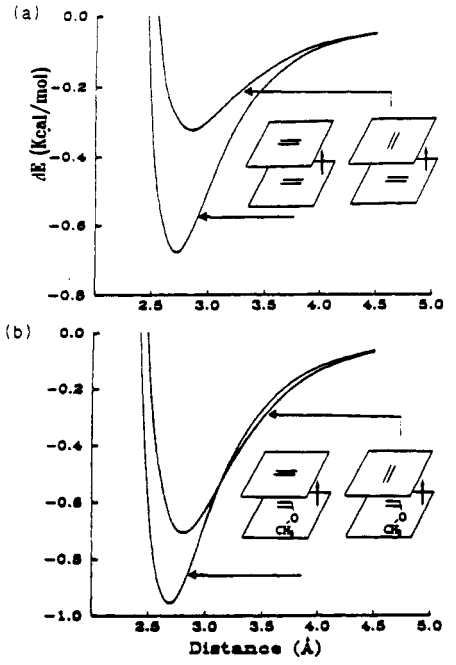

Figure 1. Stabilization energies (ΔE) of (a) ethylene dimer and (b) ethylene–MVE complex.

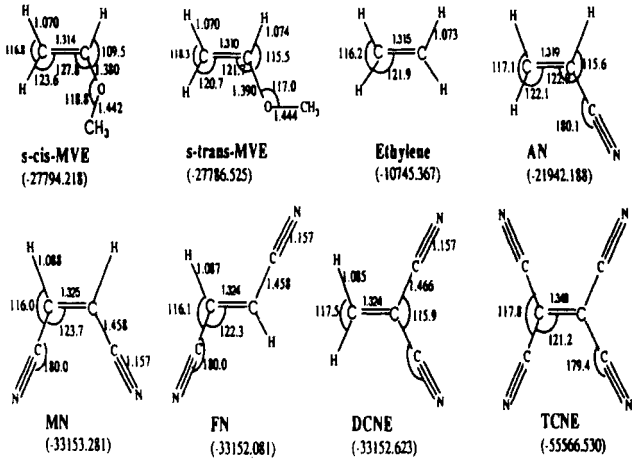

Figure 2. Geometric parameters of alkenes employed in the PVCILO calculation. (Numbers in parentheses indicate the total energy of the molecule in kilocalories per mole).

trans-MVE, from Pyckhout et al.'s work,[18] where they obtained them by ab initio calculations (4-21G basis set); AN and ethylene, from Fueno and Kamachi's work,[19] where ab initio calculations were applied (3-21G basis set); FN and MN, from Wong and Boyd's work,[20] where they calculated them with STO-3G basis set; TCNE, from the crystal structure after bond length corrections for thermal motion, studied by Drueck and Guth.[21] The geometric parameters are summarized in Figure 2.

The geometry of DA was arranged as follows to calculate the corresponding energy of DA. The plane of the MVE molecule was placed parallel to that of a cyanoethylene. The two carbon–carbon double bonds were arranged parallel or right angled and the centers of the double bonds were positioned over one another. Then, the distance between the two planes was changed, or after the distance was set, the plane of the cyanoethylene molecule was moved parallel to the double bond of MVE. We restricted our calculations only to the sets of selected geometry which might be physically meaningful to interpreted, as shown in the figures where the stabilization energy and the geometry were correlated.

Table I
Geometries of D–A Complexes and Their ΔE Values

donor	Acceptor	geometry	ΔE, kcalmol	distance, Å vertical	distance, Å horizontal
cis-MVE	AN	1	−2.01	2.6	0.0
trans-MVE		2	−2.06[a]	2.6	0.0
cis-MVE		11	−1.78	2.6	0.0
cis-MVE		12	−1.43	2.6	0.0
cis-MVE		13	−1.39	2.6	0.0
cis-MVE		14	−1.97	2.6	0.0
cis-MVE		15	−1.48	2.7	0.0
cis-MVE		16	−0.96	2.7	0.0
cis-MVE		17	−0.89	2.7	0.0
cis-MVE	MN	3	−3.30	2.5	0.0
trans-MVE		4	−2.95[a]	2.5	0.0
cis-MVE		5	−2.06	2.6	0.0
trans-MVE		6	−2.37[a]	2.6	0.0
cis-MVE		18	−2.61	2.6	0.0
cis-MVE		19	−1.94	2.6	0.0
cis-MVE	FN	7	−2.80	2.5	0.0
trans-MVE		8	−3.07[a]	2.5	0.0
cis-MVE		9	−2.45	2.5	0.0
trans-MVE		10	−2.19[a]	2.5	0.0
cis-MVE		20	−2.81	2.6	0.0
cis-MVE		21	−1.87	2.6	0.0
		22	−2.64	2.5	0.0
cis-MVE	DCNE	23	−2.29	2.6	0.0
		24	−3.06	2.5	0.0
		25	−1.24	2.7	0.0
cis-MVE	TCNE	26	−4.05	2.5	0.0
		27	−3.90	2.5	0.0
cis-MVE	MN	29	−28.1	1.9	1.6
cis-MVE	DCNE	31	−33.6	1.9	1.7
cis-MVE	TCNE	28	−28.3	1.9	1.7
cis-MVE	TCNE	30	−35.7	1.9	1.6

[a] Although some of these values are higher than those of the corresponding cis compound, note that *trans*-MVE is less stable than *cis*-MVE (see text).

We selected energy calculated using third-order Moller–Plesset–Rayleigh–Schrodinger theory in the PVCILO calculations for our discussion. The stabilization energy (ΔE) was obtained from the energy difference between the energy of the DA, E_{DA}, and the energies of separated D and A, E_D and E_A.

$$\Delta E = E_{DA} - (E_D + E_A)$$

ΔE for each given geometry of the DA complex is given in Table I, and the total energy values of each molecule calculated using PVCILO are also included in Figure 2.

3. Results and Discussion

3.1. Effect of Configuration of MVE. Because three stable conformations of MVE, s-cis, s-gauche, and s-trans, are present, we determined whether any conformer forms a more stable DA over the other one or not before calculating the stabilization energies of DA between MVE and the cyanoethylenes. The s-cis conformation is more stable than s-gauche by 1.9–2.2 kcal/mol, and the gauche is more stable than the s-trans by 0.02–0.15 kcal/mol.[17,22-26] The abundance of the s-cis is 88% (95%[18]) and s-gauche 12% at 27 °C.[22] According to our PVCILO calculations, however, the energy difference between the *s-cis* and *s-trans*-MVE is 7.69 kcal/mol (Figure 2).

The difference in the stabilization between the complexes, *s-cis*-MVE–AN (complex 1 in Figure 3a) and *s-trans*-MVE–AN (complex 2) is −7.64 kcal/mol, which is practically equivalent to the difference in *s-cis*- and *s-trans*-MVE (−7.69 kcal/mol) themselves. We deduce

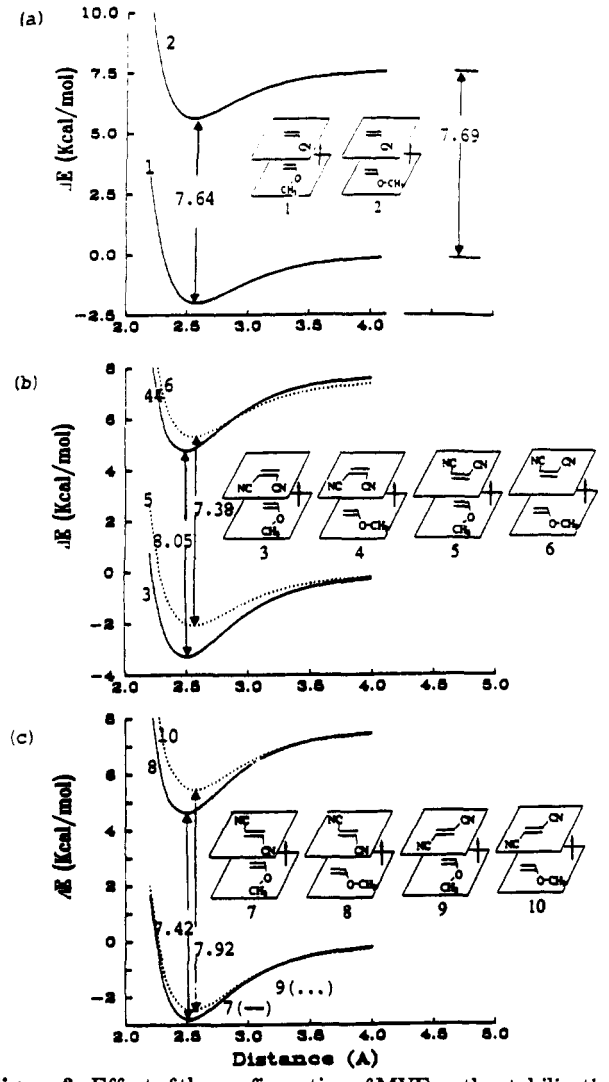

Figure 3. Effect of the configuration of MVE on the stabilization energy (ΔE) of the complexes: (a) AN–MVE; (b) MN–MVE; (c) FN–MVE.

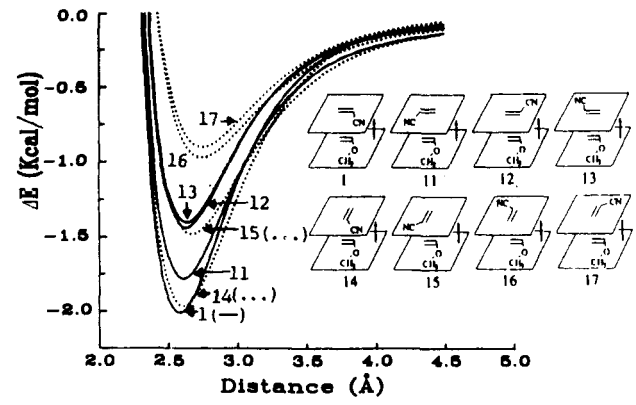

Figure 4. Stabilization energies (ΔE) and various geometries of AN–MVE complex.

from this result that the *s-cis*- and *s-trans*-MVE have the same capability to form DA with AN. Because MVE is present mainly in the s-cis form, we may conclude that MVE forms a complex with AN in the s-cis form.

In the cases of MN and FN, two different geometries of the DA were considered. As shown in Figure 3b, *s-trans*-MVE forms a weaker DA with MN than *s-cis*-MVE in the complexes **6** and **5**, whereas *s-trans*-MVE forms a stronger DA in the geometries of complexes **4** and **3**. These orders are reversed, however, when FN–MVE complexes are considered (Figure 3c).

s-trans-MVE forms a stronger DA than *s-cis*-MVE in complexes **8** and **7**, whereas *s-trans*-MVE forms a weaker DA than *s-cis*-MVE in the complexes **10** and **9**. Although these results show a small change in the stabilization energy due to the configuration of MVE, the difference in the stabilization energy between the DA of the s-cis and s-trans with MN and FN varies significantly compared with that between *s-cis*- and *s-trans*-MVE. Therefore, we conclude that MVE is present predominantly in the s-cis configuration when it forms DA with cyanoethylenes and the ratio of the s-cis to the s-trans does not change with the formation of DA; consequently, we employed only the s-cis form of MVE in further calculations. The results also suggest that *s-cis* and *s-trans*-MVE have the same ability to form DA with cyanoethylenes. Since the energy of *s-gauche*-MVE is almost the same as that of the *s-trans*, we believe that the resulting DA formed with the s-gauche will be almost the same as those formed with the s-trans in terms of energy.

3.2. ΔE of DA When the C–C Double Bonds Are Parallel or Right-Angled. Eight sets of geometries were examined for AN–MVE complex formation (Figure 4). Of the eight sets, complex 1 in which the cyano group of AN is positioned on the same side with the methoxy group of MVE has a maximum stabilization energy (ΔE = −2.01 kcal/mol) at the equilibrium distance of 2.6 Å. It is also notable that the equilibrium distances also varied from 2.6 to 2.7 Å with various complexes. If complex 1 is compared with complex 11, where the cyano group is positioned on the opposite side of the methoxy group, the energy difference between the two complexes is 0.23 kcal/mol. This indicates that the cyano group of AN interacts with the methoxy group of MVE rather than repels the methoxy group when they come closer together. Since the energy difference between the two is small (0.23 kcal/mol), it may be possible that the copolymer obtained from AN and MVE would not possess regioselectivity and would have a mixed structure of head-to-tail and head-to-head sequences. One should be cautious, however, in drawing this conclusion because the transition state is not known; in other words, the kinetic parameters of the copolymerization are not known. Interestingly, complex 14 possesses almost the same degree of stabilization energy as complex 1. Of course, there may be other geometries which possess lower ΔE values than the eight geometries of the AN–MVE complexes examined here.

The stabilization energies of the complexes of MVE with other cyanoethylenes, FN, MN, DCNE, and TCNE, were calculated for similar geometries as those used in our study of the AN–MVE complex. The energy profiles of the complexes are shown in Figure 5. It is evident from these energy profiles that MVE forms complexes with these cyanoethylenes and the stabilization energies are in the range 2.80–4.05 kcal/mol for the complexes possessing the geometries shown. These values are well within the range of the reported values for the formation of donor–acceptor complexes, from small values[27] to 5–10 kcal/mol.[28] The distance between MVE and the cyanoethylenes is about 2.5 Å in these complexes. Since van der Waals complexes might be expected to have carbon–carbon distances of about 3.2 Å, or greater (ethane dimer, 3.75 Å),[14] the shortened distances are further evidence of the formation of DA.

The calculations on the complexes of MN–MVE and FN–MVE were briefly discussed in a previous paper.[29] Among four geometries considered for the MN–MVE complex, complex 3 is the most stable (ΔE = −3.30 kcal/mol) and the equilibrium distance between MN and MVE

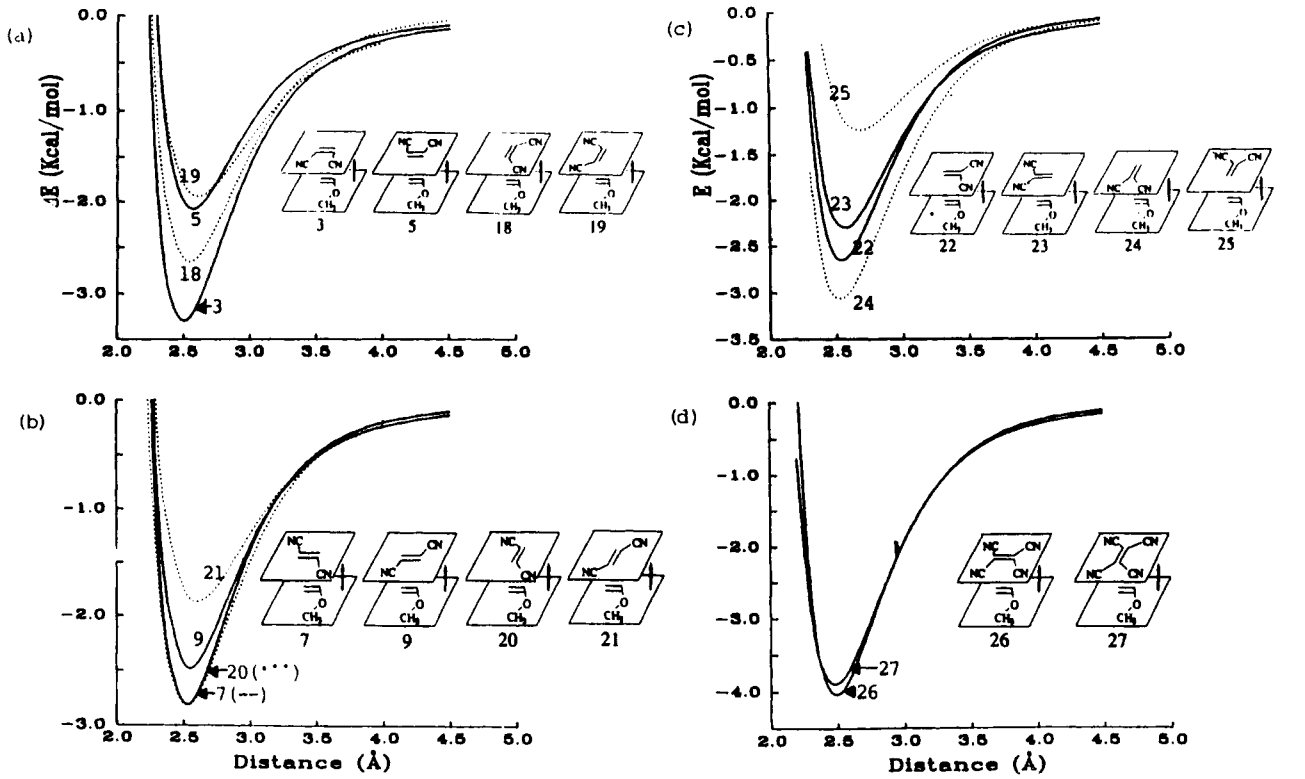

Figure 5. Stabilization energies (ΔE) of MVE complexes with (a) MN, (b) FN, (c) DCNE, and (d) TCNE.

is 2.5 Å (Figure 5a). Comparison of complex **3** with **5** reveals that the difference in their stabilization energies is 1.24 kcal/mol. This difference gives the ratio of the value for complex **3** to the value for complex **5** equal to 8.1 at 25 °C, which suggests that the MN–MVE complex exists mainly as complex **3** rather than complex **5**. As was discussed in previous papers,[1,29] complex **3** would preferentially participate in the copolymerization. Similarly, we observed an MN–MVE complex, complex **18** where the C–C double bonds are cross-overlapped, which is more stable than complex **5**, where the C–C double bonds are fully overlapped with each other. Again we caution that these results, strictly speaking, are for gas-phase reactions, but we do not believe that solvent interactions would have such effects.

Complexes **7** and **20** in Figure 5b possess almost the same stabilization energies (−2.8 kcal/mol at 2.5 Å) and are the most stable complexes among the four complexes examined. The difference in the stabilization energies between complexes **7** and **9** is less than 0.4 kcal/mol, and the corresponding population ratio of complex **7** to complex **9** is 1.8 at 25 °C. Therefore, we predict that both complexes exist and participate in the FN–MVE copolymerization. Consequently, even when the DA alone participates in the copolymerization, it may be difficult to obtain a stereoregular copolymer as we anticipated before.[1] Because MN forms a stronger complex with MVE (ΔE = −3.30 kcal/mol) than FN does (−2.81 kcal/mol) and because of the difference in the population ratios of the complexes in each case, it is predicted that MN should form a more stereoregular copolymer with MVE than FN.

In the case of the DCNE–MVE complexes (Figure 5c), complex **24** is more stable than complex **22** by 0.42 kcal/mol. These results further suggest that the role of the cyano groups is important to DA formation, and it is not necessary that the C–C double bonds be overlapped to form the most stable complex. However, the stabilization energy of complex **24** is only −3.08 kcal/mol and may not be sufficient for the observed spontaneous reaction

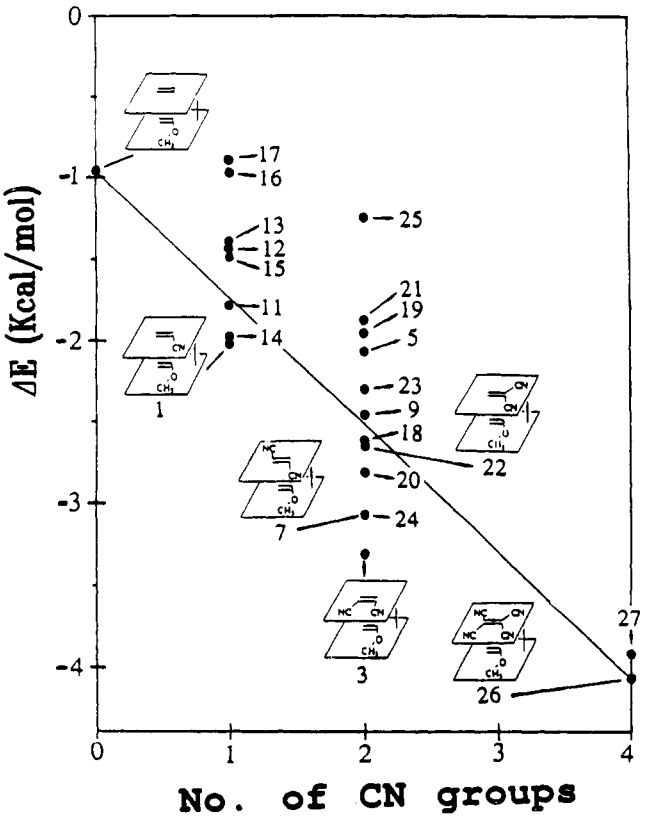

Figure 6. Relationship of ΔE with the number of cyano groups when the C–C double bonds of MVE and cyanoethylenes overlap directly parallel or right angles.

between DCNE and MVE at 25 °C, which suggests a search for another complex geometry which might have a higher stabilization energy. We will discuss this point later.

Complexes **26** and **27** in Figure 5d possess almost the same stabilization energies, 4.05 and 3.90 kcal/mol at 2.5 Å, respectively. These are the highest values observed among the cyanoethylene–MVE complexes. However, the

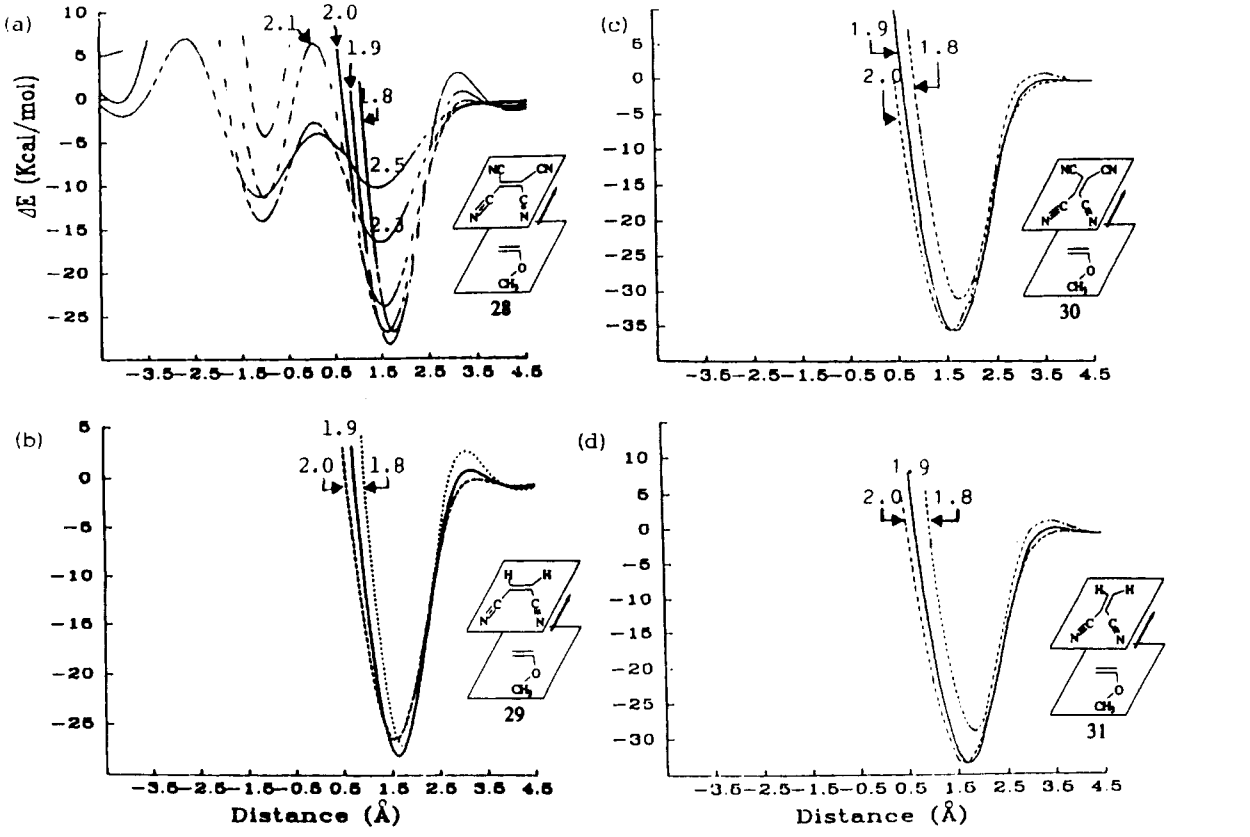

Figure 7. Stabilization energies (ΔE) of MVE complexes with (a) TCNE, (b) MN, (c) TCNE, and (d) DCNE.

values may be again too small to explain the spontaneous reaction between TCNE and MVE, which was mentioned under Introduction.

As shown in Figure 6 (see also Table I), ΔE is increased as the number of cyano groups in ethylene is increased. Only the complex geometries in which the C–C double bond of the cyanoethylenes are arranged parallel or at right-angles directly over the C–C double bond of MVE have been studied so far.

3.3. ΔE of DA When the C–C Double Bonds Are Not Overlapped Directly. The values of ΔE, however, may be again too small to explain the spontaneous reactions between TCNE and MVE and DCNE and MNE which were mentioned under Introduction. Since it is evident from these results that cyano groups contribute to the stabilization of the complexes, we speculated that the complex might be more stable if the geometry was so arranged to utilize the π orbitals of the cyano groups in addition to C–C double bonds to form the complex with MVE. Therefore, we considered other geometries for the complexes. To this purpose, the height between the planes of cyanothylenes and MVE molecules was set and the plane of the cyanoethylenes was moved over the plane of the MVE molecule to get maximum stabilization energy. We reexamined ΔE of MN, DCNE, and TCNE complexes after changing the geometries, and the results are shown in Figure 7.

Figure 7a shows energy profiles of the TCNE–MVE complexes when the distance between the planes of the two molecules were set and the plane of the TCNE molecule was moved parallel over the plane of the MVE molecule. As the plane is moved, four different geometries become stable at the horizontal distances between the two C–C double bonds of 4.0, 1.7, −1.1, and −4.0 Å, respectively (a minus sign indicates the plane of TCNE was moved in the opposite direction to the plus direction). The geometry at 1.7 Å has the highest ΔE, −28.3 kcal/mol, among the four. This ΔE is substantially higher than those of complexes **26** and **27**, and this high ΔE may induce the spontaneous reaction between TCNE and MVE. Consequently, it is predicted that the complex of this geometry is predominant over those formed by a direct overlapping of the C–C double bonds. The top view of this complex is shown in Figure 8a.

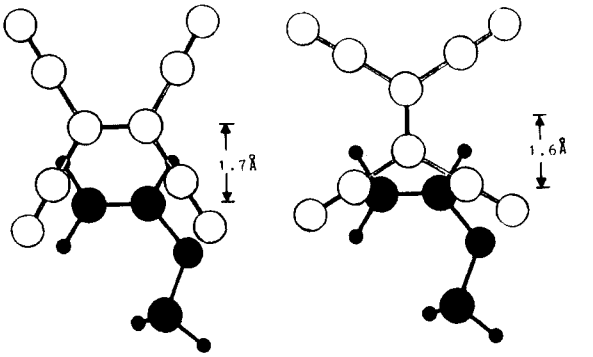

Figure 8. Top views of the geometries of the TCNE–MVE complexes possessing the highest ΔE when the double bonds are (left) parallel and (right) 90° angled.

This geometry shows that the complex utilizes the maximum delocalization of the π orbitals of C–C double bonds and C–N triple bonds. The direct distance between the two double bonds is 2.55 Å ($=(1.7^2 + 1.9^2)^{1/2}$) and the angle is 48°. These data indicate that the two molecules become closer (1.7 Å) than the complexes **26** and **27** (2.50 Å) without sacrificing the distance between the C–C double bonds (2.55 vs 2.50 Å).

In a similar procedure, ΔE for the MN–MVE complex was calculated (Figure 7b). It shows that the complex has a maximum ΔE, −28.1 kcal/mol at a vertical distance of 1.9 Å and a horizontal distance of 1.6 Å, these values are nearly identical to those obtained from TCNE–MVE complex in Figure 7a. It is notable, however, MN does

not react spontaneously with MVE at room temperature, although ΔE is comparable to that of the TCNE–MVE complex.

Because it was found from complexes **28** and **29** that full overlap of the C–C double bonds was not necessarily required to obtain a maximum ΔE, we reexamined the TCNE–MVE and DCNE–MVE complexes, complexes **27** and **24**, respectively, to find out whether or not these complexes have lower ΔE by moving the plane of one molecule after setting the vertical distance as in the case of complexes **28** and **29**. In Figure 7c,d the planes of TCNE and DCNE were rotated 90° and the planes were moved as in the same manner employed in Figure 7a,b.

The highest ΔE, −35.7 kcal/mol, for the TCNE–MVE complex was obtained when the vertical distance between two planes is 1.9 Å and the center of the double bonds separated by 1.6 Å horizontally. This geometry is shown in Figure 8b, and this geometry possesses a higher ΔE by 7.4 kcal/mol than the one shown in Figure 8a. This result reveals that this geometry is the most stable one among the geometries considered for complexes **26–28** and **30**. Therefore, we believe that the geometry when TCNE reacts with MVE spontaneously is closer to the one shown in Figure 8b rather than the one shown in Figure 8a, where the C–C double bonds are parallel. It may consequently be interesting to find the geometry of the complexes which have the highest ΔE values among all the possible geometries, although we have restricted the geometries to those we have described here.

The DCNE–MVE complex possesses a maximum ΔE, −33.6 kcal/mol, when the plane is separated by 1.9 Å and the center of the C–C double bonds by 1.7 Å (Figure 7d). The complex of this geometry possesses much greater ΔE than the one considered in Figure 5c. Therefore, it is believed that DCNE reacts spontaneously with MVE by forming (or approaching) this type of DA first.

In conclusion, we calculated the most stable geometries of several cyanoethylene–MVE complexes and correlated them with their reaction and the stereoregularity of the products. We did not try to find the most stable geometry among all possible geometries. We rather calculated the most stable geometry among the sets of selected geometries. The PVCILO calculation reveals that MVE and cyanoethylenes form stable complexes when the C–C double bonds overlap each other and a specific geometry possesses a higher ΔE than others. We therefore speculate that the specific geometry of DA causes the stereoregularity in copolymers derived from DA. The results further reveal that maximum stabilization energies are obtained by utilization of the π-orbitals of the cyano groups. Thus, for instance, complex **29** is much more stable than complex **3**. As we mentioned before, since the calculations do not show the transition states of DA, it may not be possible to correlate ΔE with reaction modes directly. Further, well-defined calculations are needed to prove the exact reaction mode which would lead to spontaneous reaction or would form homopolymer, copolymer, or cycloadducts.

Acknowledgment. We are pleased to acknowledge financial support of this research program by the Polymers Division of Materials Research, National Science Foundation, through Grant NSF/DMR 84-15072.

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