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Supplementary Material

SCRF/Monte Carlo Study of Solvent Effects on a Polar [2+2] Cycloaddition

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Computed CHELPG and Mulliken charges of the reactants, intermediate, and transition structures from RHF/6–31G* and Becke3LYP/6–31G* calculations are given in Figures 1–7. Computed charges from the SCIPCM RHF/6–31G* single–point calculations are shown in Figures 8–9. FEP results for gas–phase to solvent–adapted geometries and charges of the reactants and transition structures are illustrated in Figures 10–12. Finally, RHF/6–31G* optimized geometries of the product are given in Figure 13 and electronic energies for the optimal structures are given in Table I.

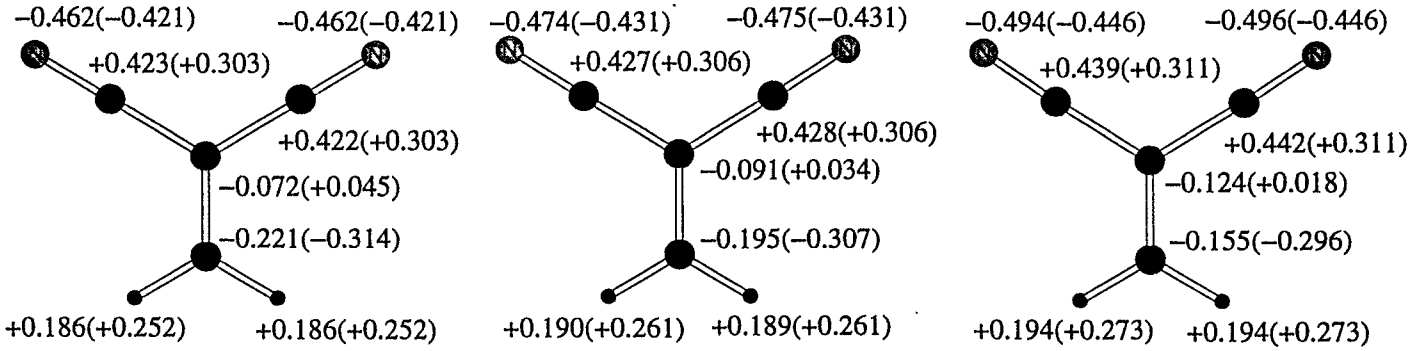
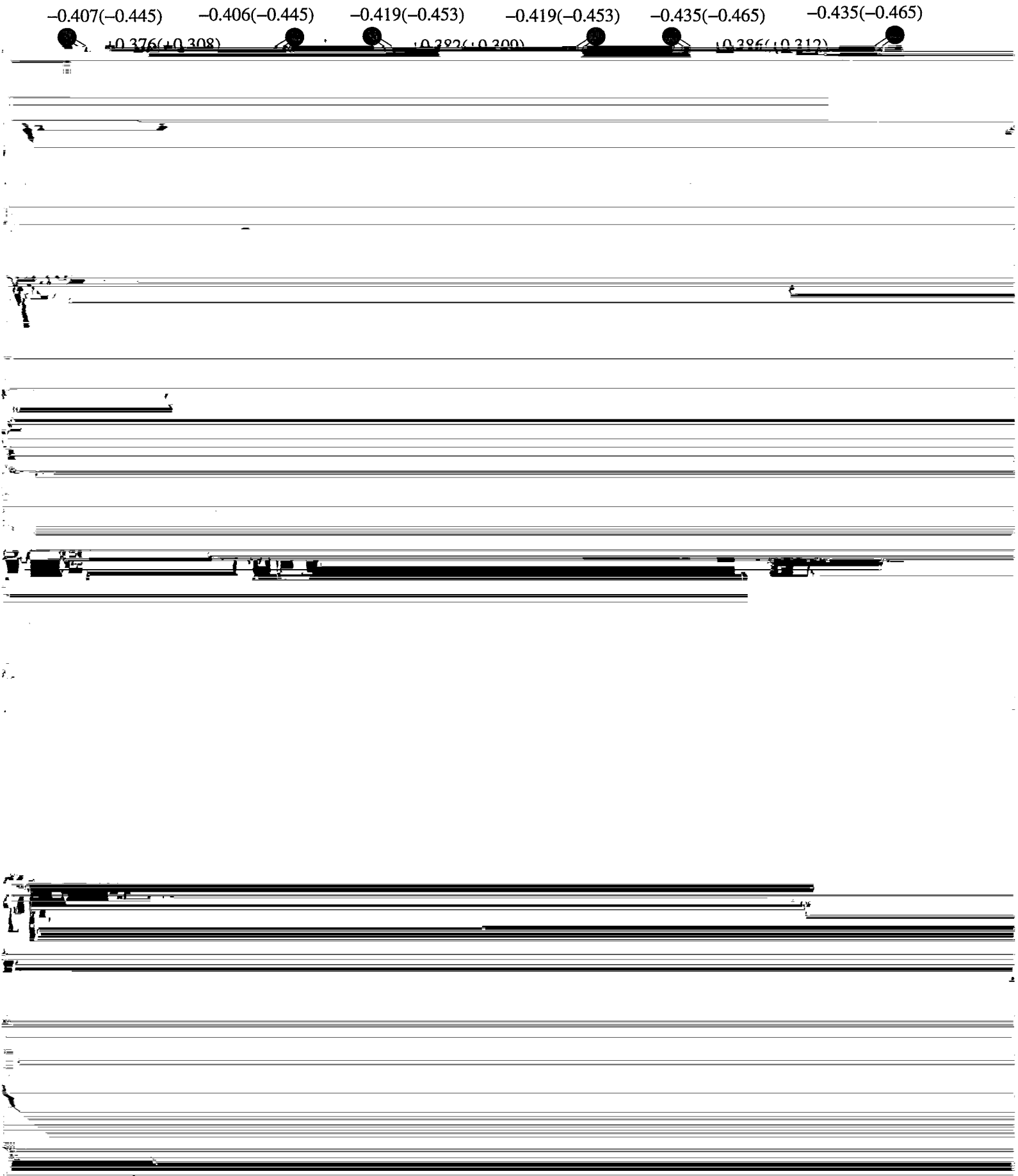


Figure 1. Computed CHELPG and Mulliken (in parentheses) charges for 1,1–dicyanoethylene from the RHF/6–31G* calculations.


−0.407(−0.445)
−0.406(−0.445)
−0.419(−0.453)
−0.419(−0.453)
−0.435(−0.465)
−0.435(−0.465)
+0.376(+0.308)
+0.382(+0.309)
+0.386(+0.312)
+0.163(+0.205)
+0.163(+0.205)
+0.167(+0.213)
+0.167(+0.213)
+0.173(+0.225)
+0.173(+0.225)

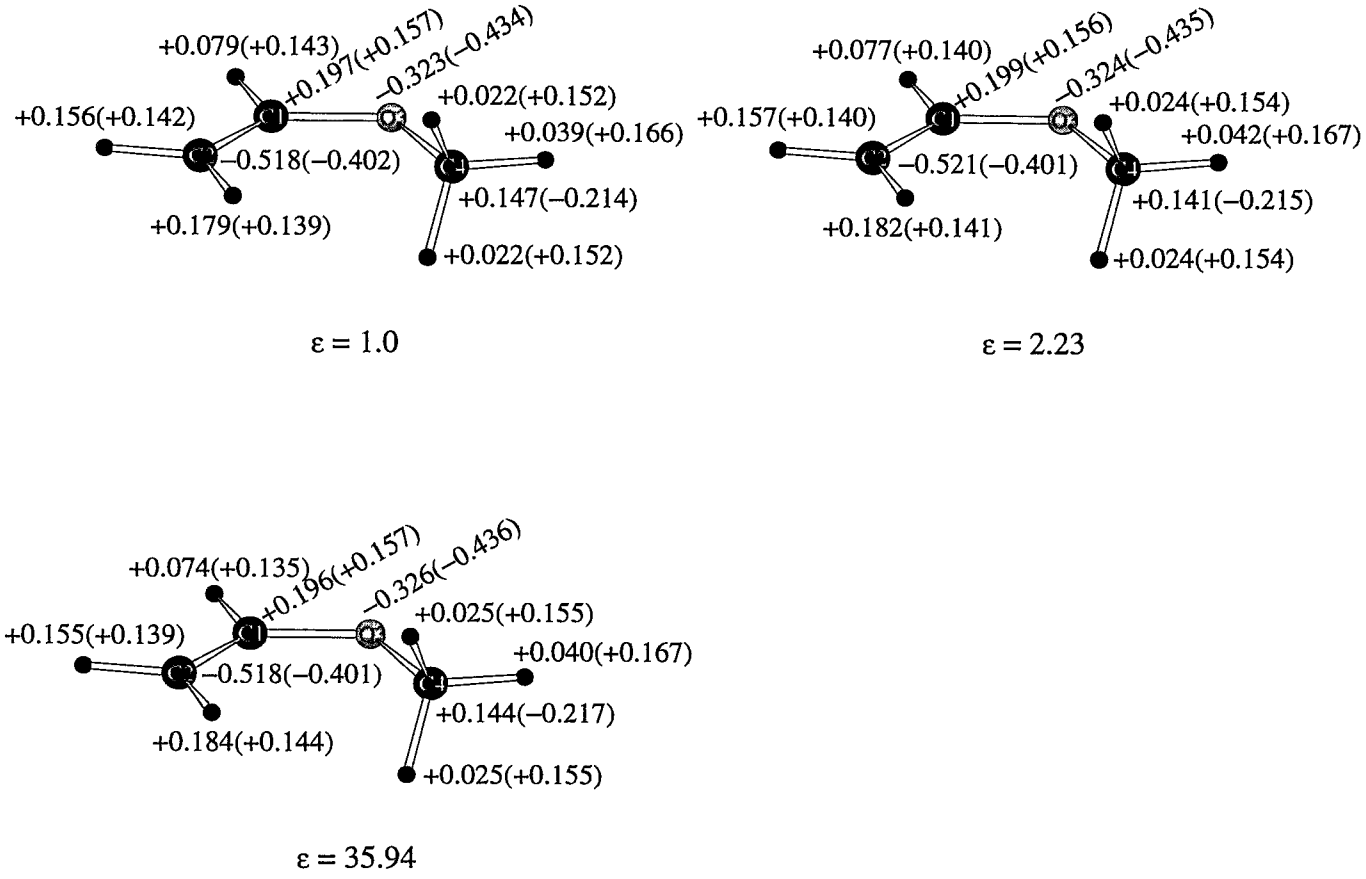


Figure 4. Computed CHELPG and Mulliken (in parentheses) charges for the *s−cis* conformer of methyl vinyl ether from the Becke3LYP/6−31G* calculations.

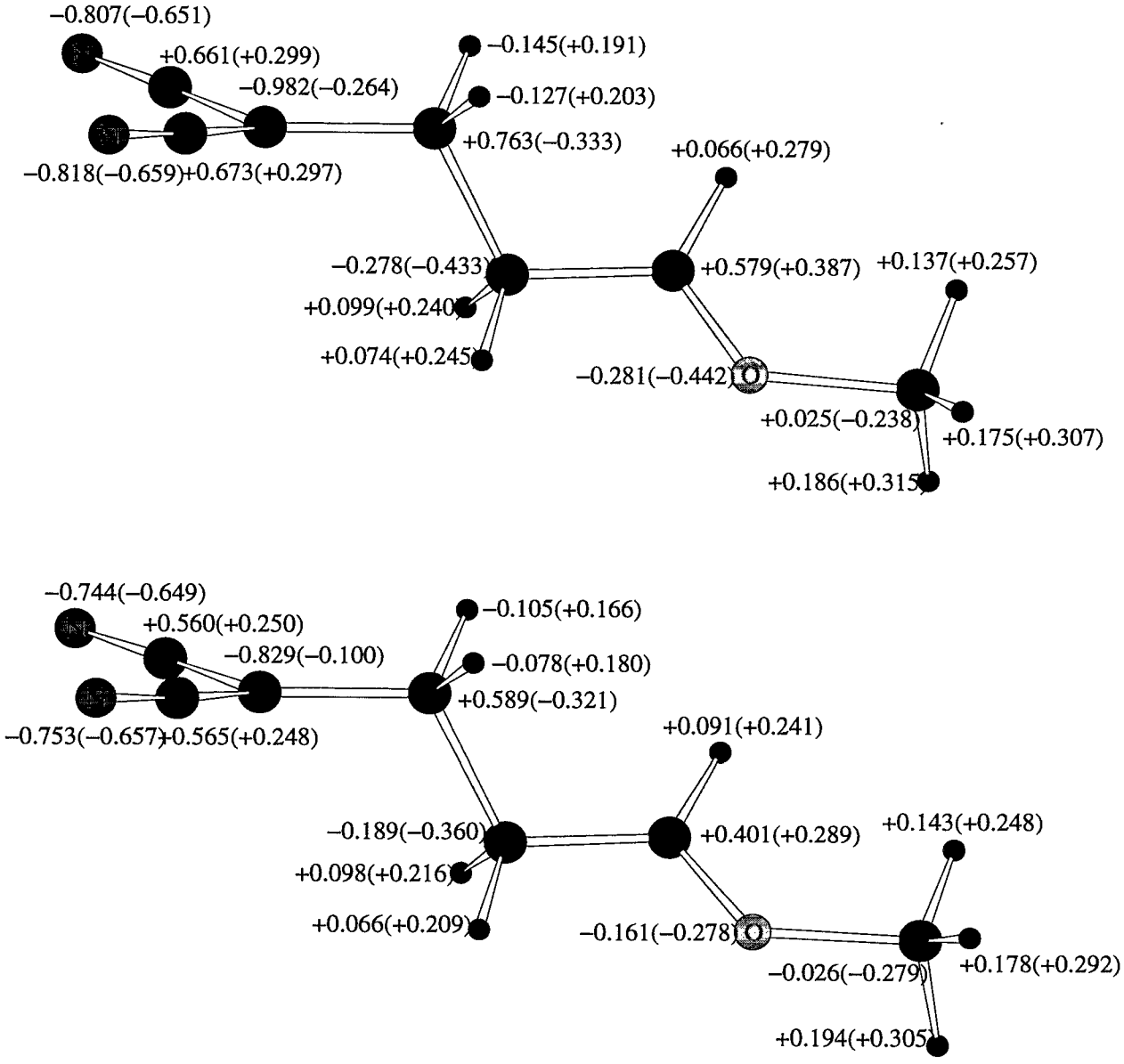


Figure 5. Computed CHELPG and Mulliken (in parentheses) charges for the intermediate from the RHF/6−31G* (top) and Becke3LYP/6−31G* (bottom) calculations at $\varepsilon = 35.94$.

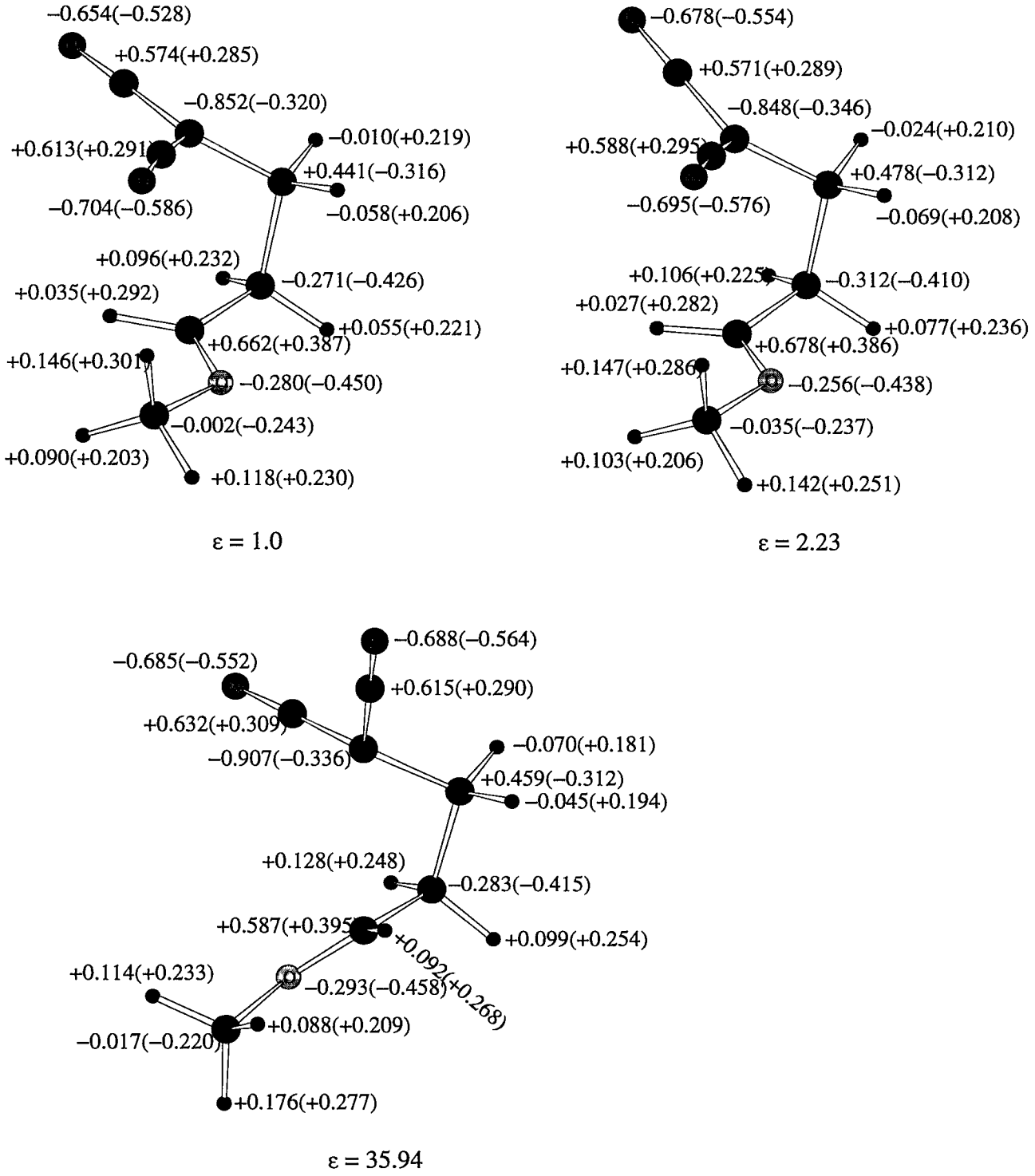


Figure 6. Computed CHELPG and Mulliken (in parentheses) charges for the minimum energy conformers of the transition state in the [2+2] reaction of DCNE and MVE from the RHF/6–31G* calculations.

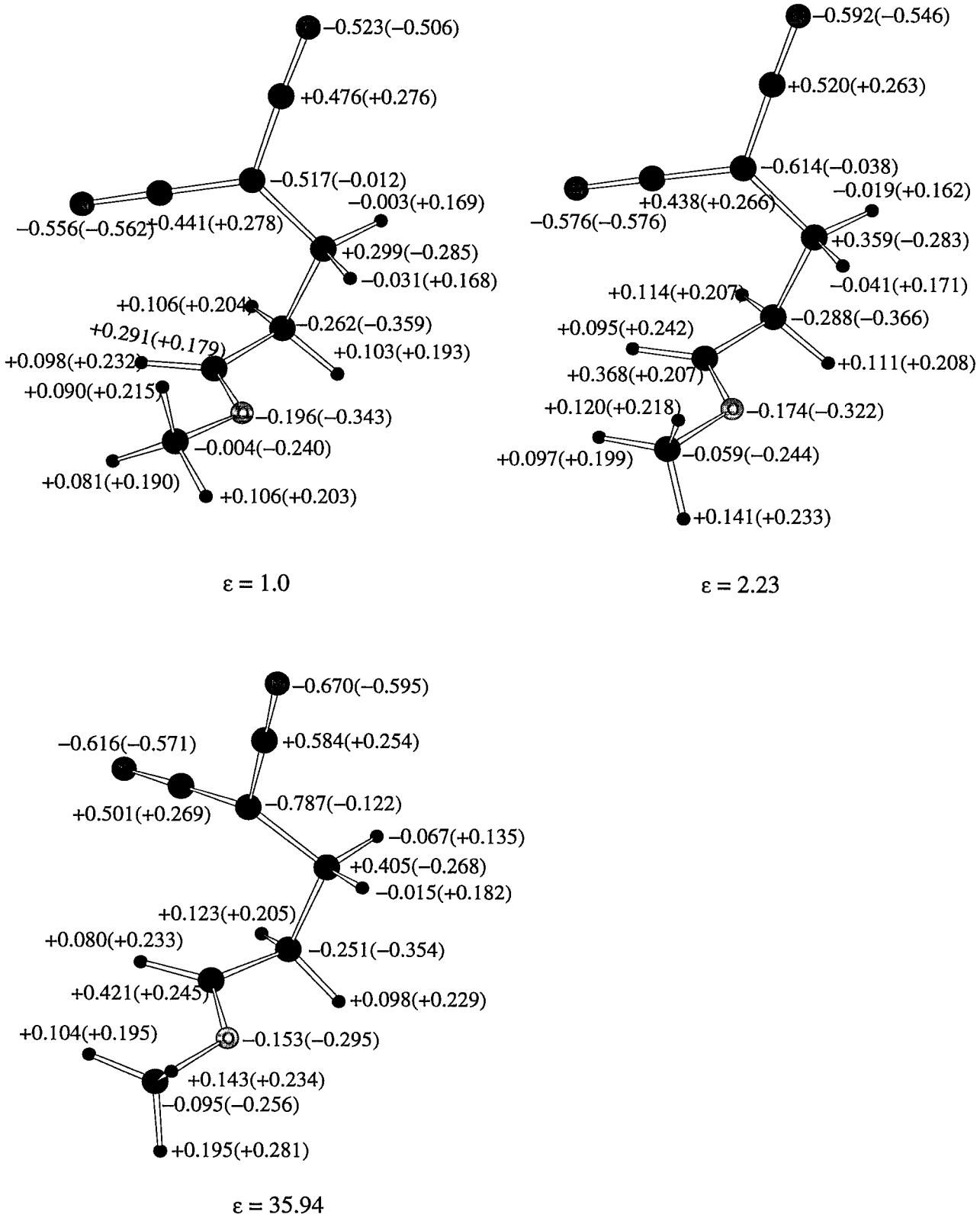
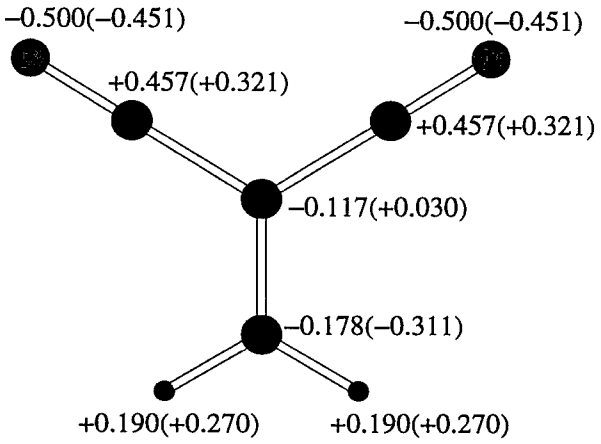
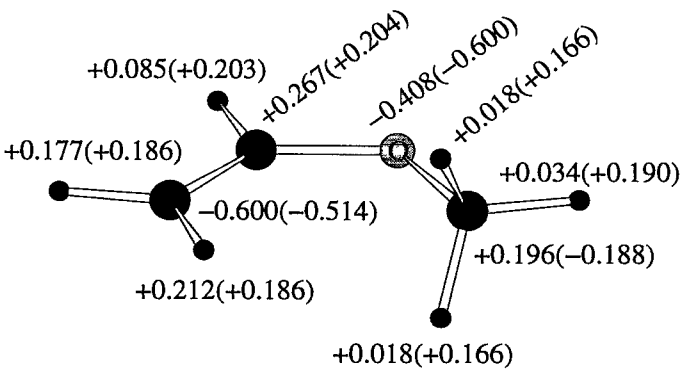


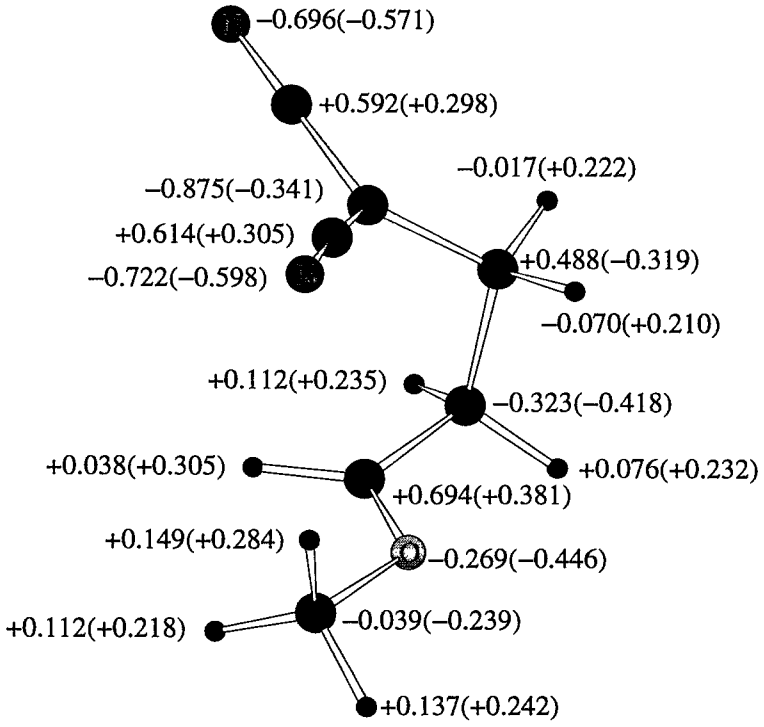
Figure 7. Computed CHELPG and Mulliken (in parentheses) charges for the minimum energy conformers of the transition state in the [2+2] reaction of DCNE and MVE from the Becke3LYP/6–31G* calculations.



DCNE

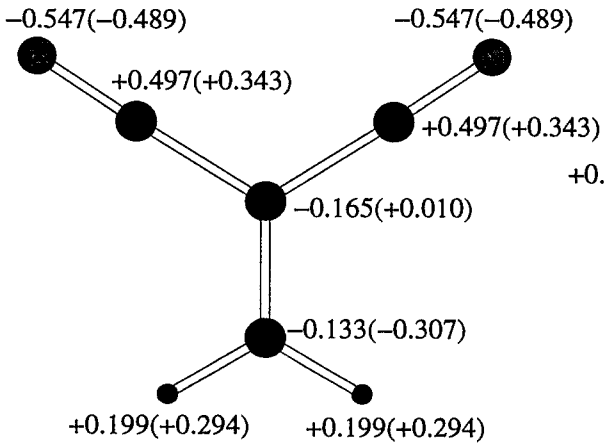


MVE

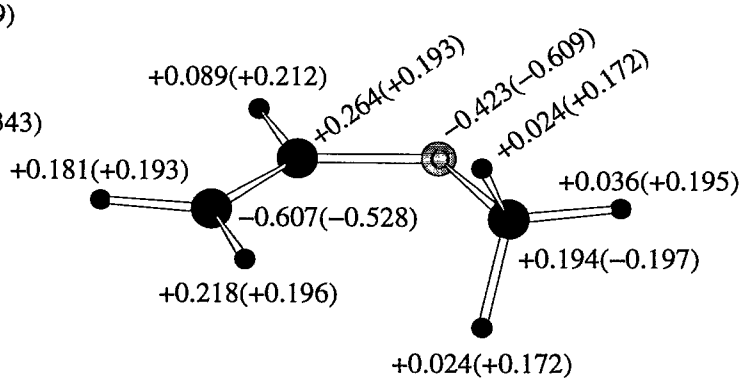


TS

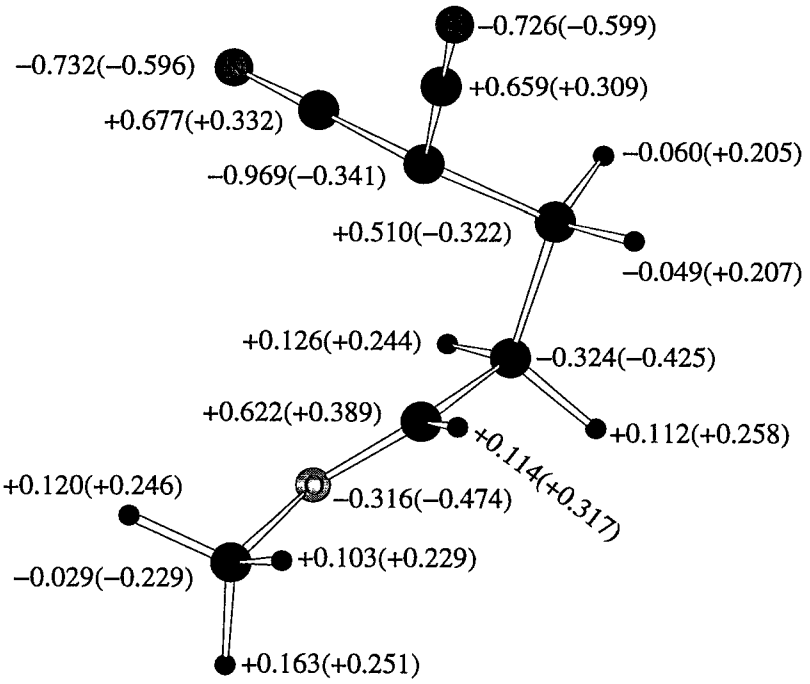
Figure 8. Computed CHELPG and Mulliken (in parentheses) charges for the minimum energy conformers of the reactants and transition state from the SCIPCM RHF/6–31G* calculations at $\varepsilon = 2.23$.



DCNE



MVE



TS

Figure 9. Computed CHELPG and Mulliken (in parentheses) charges for the minimum energy conformers of the reactants and transition state from the SCIPCM RHF/6–31G* calculations at $\varepsilon = 35.94$

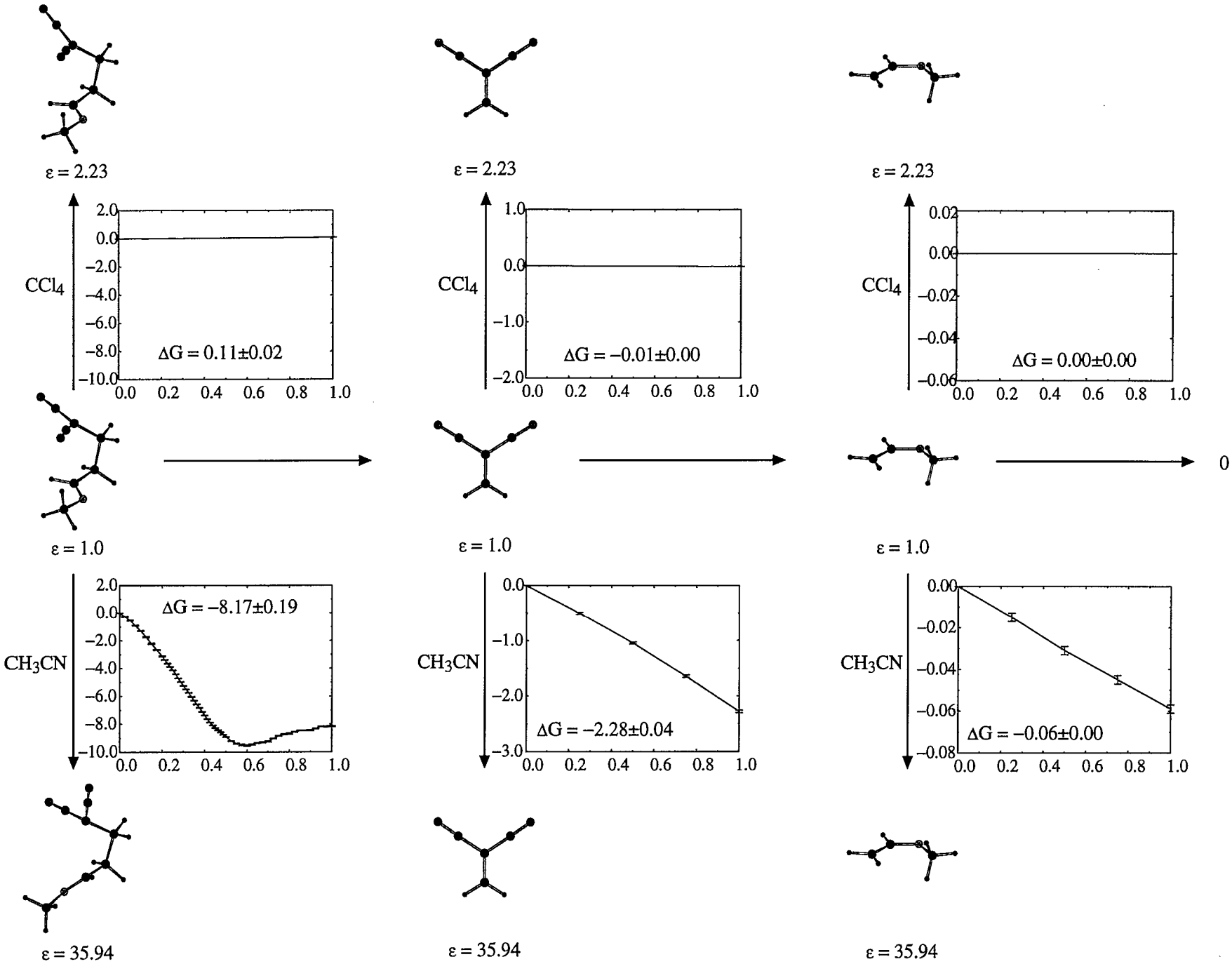


Figure 10. FEP results for the perturbation of RHF/6–31G* gas–phase to solvent–adapted geometries and charges of the TS, DCNE, and MVE.

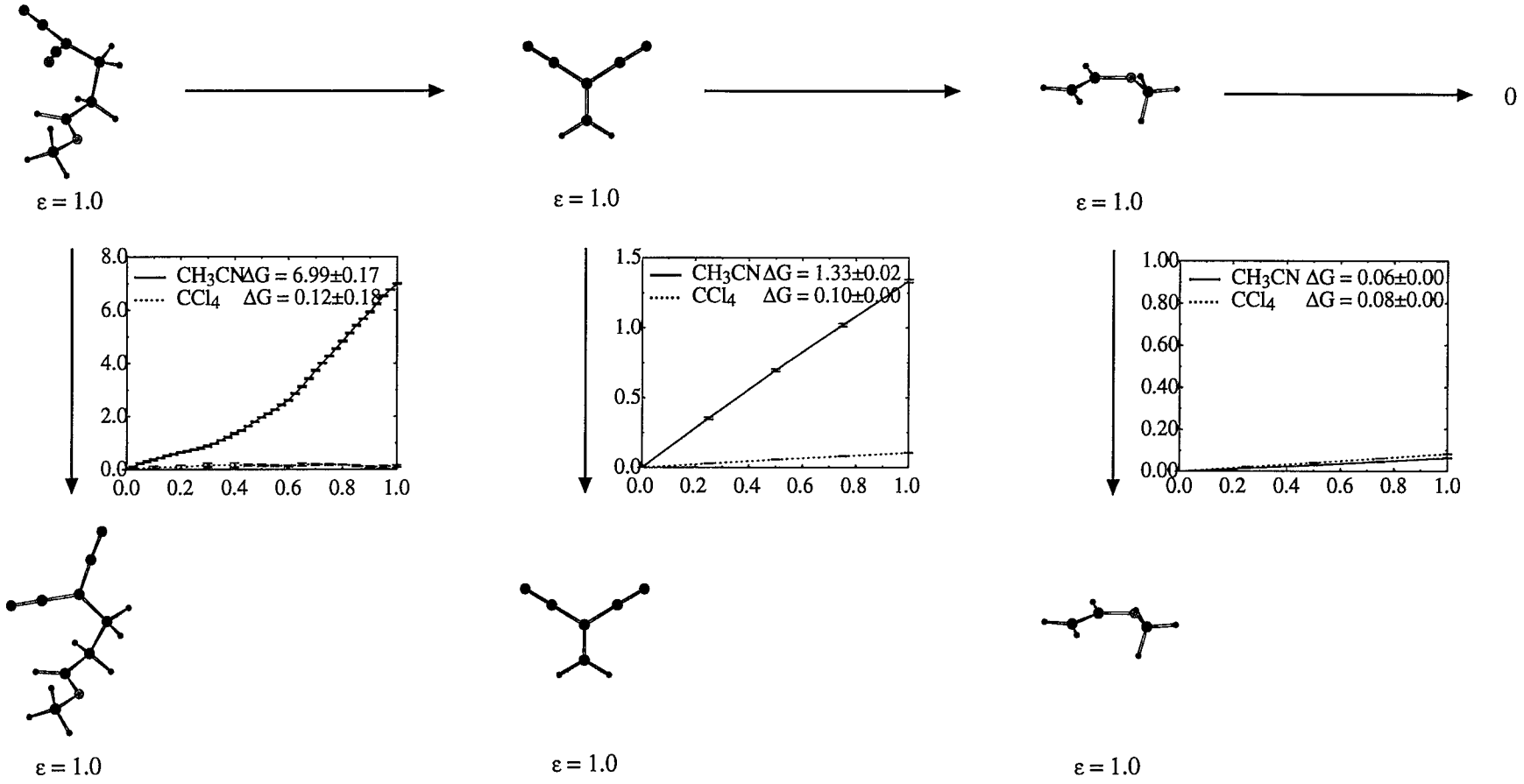


Figure 11. FEP results for the perturbation of gas–phase RHF/6–31G* to Becke3LYP/6–31G* geometries and charges of the TS, DCNE, and MVE.

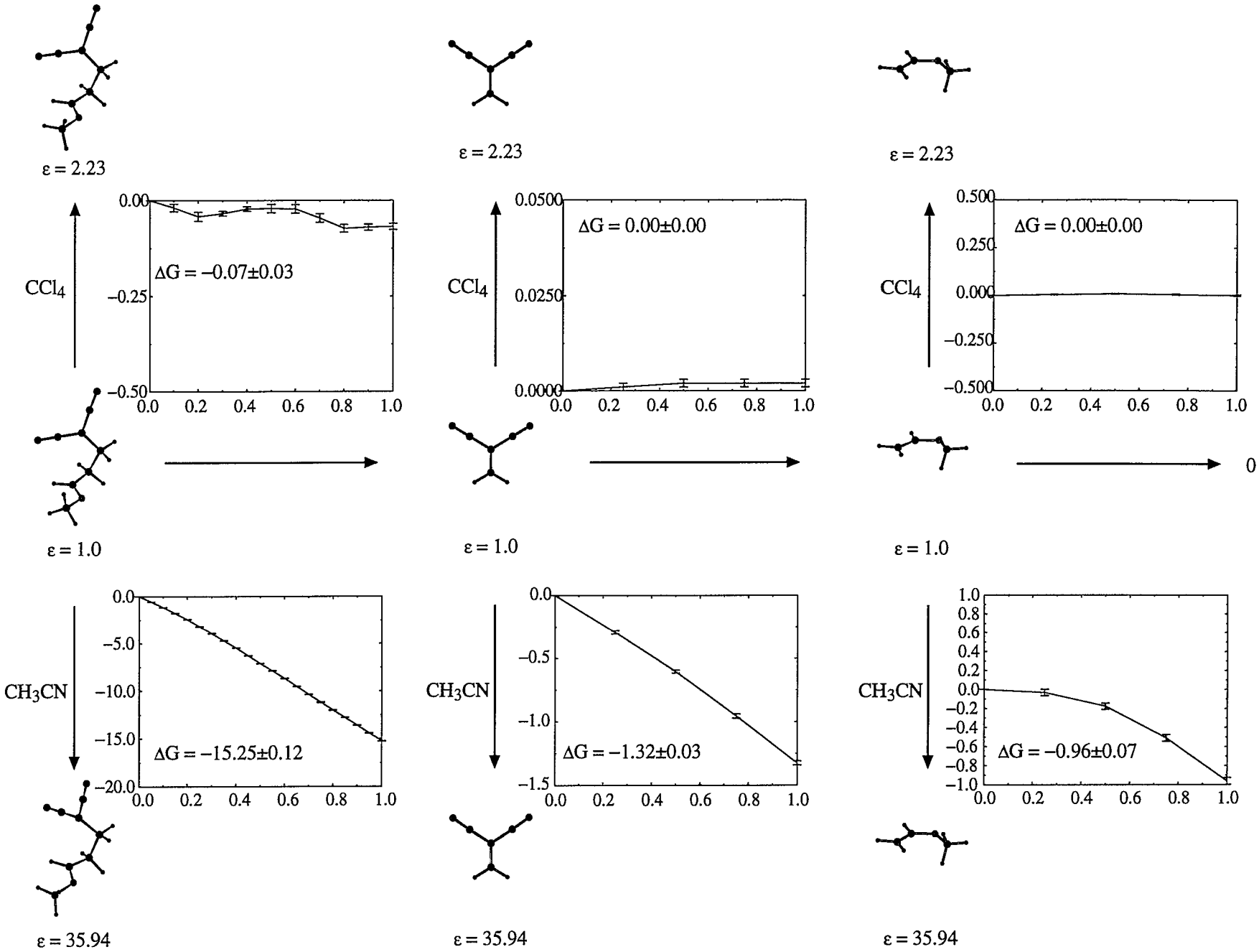


Figure 12. FEPresults for the perturbation of Becke3LYP/6–31G* gas–phase to solvent–adapted geometries and charges of the TS, DCNE, and MVE.

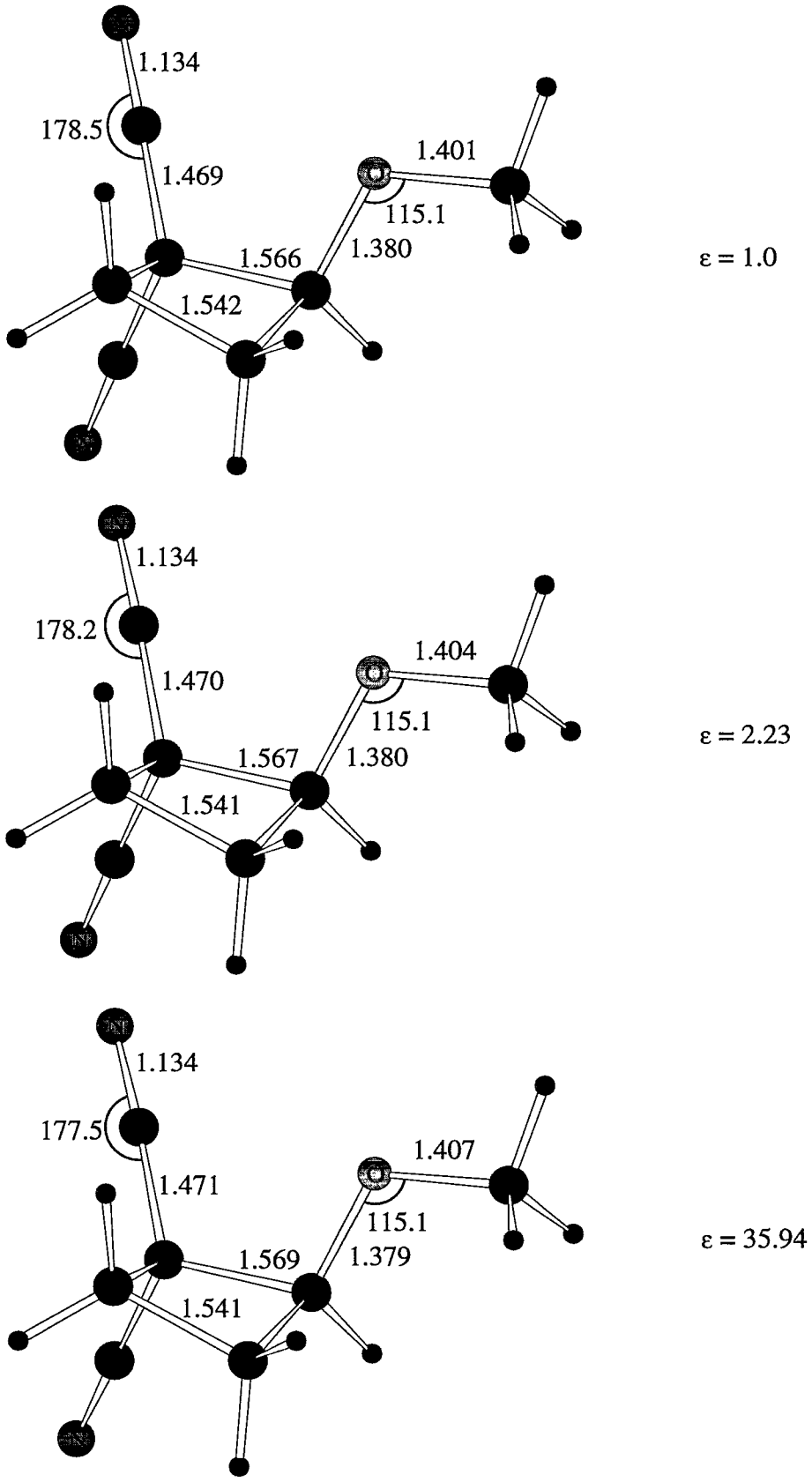


Figure 13. RHF/6–31G* optimized geometries of the product at ε = 1.0, 2.23, and 35.94

Table I. Total Electronic Energies (a.u.) of the Structures in the [2+2] DCNE + MVE Reaction[a]

ε	structure		RHF/ 6-31G*	MP2/6-31G*// RHF/6-31G*	B3LYP/ 6-31G*
	DCNE		–261.49054	–262.28931	–263.06267
		s-cis	–191.91594	–192.47403	–193.11404
	MVE	*skew*	–191.91278		
		s-trans	–191.91272		
1.0					
		endo-cis	–453.35213		
	TS	*endo-trans*	–453.35738	–454.72273	
		exo-cis	–453.34736		
		exo-trans	–453.35789	–454.72280	–456.13691
	product		–453.43058	–454.80504	–456.19798
	DCNE		–261.49311	–262.29127	–263.06468
		s-cis	–191.91606	–192.47415	–193.11418
	MVE	*skew*	–191.91319	–192.46998	
		s-trans	–191.91316		
2.23					
		endo-cis	–453.36401		
	TS	*endo-trans*	–453.36788	–454.73072	
		exo-cis	–453.36286		
		exo-trans	–453.36927	–454.73250	–456.14651
	product		–453.43322	–454.80735	
	DCNE		–261.49673	–262.29406	–263.06747
		s-cis	–191.91621	–192.47433	–193.11429
	MVE	*skew*	–191.91375	–192.47047	
		s-trans	–191.91374		
35.94	intermediate		–453.42270	–454.77973	-456.19437
		endo-cis	–453.38888		
	TS	*endo-trans*	–453.38948	–454.75608	
		exo-cis	–453.38480		
		exo-trans	–453.38906		–456.17057
	product		–453.43682	–454.81055	–456.20346

[a]Results in all Tables at ε = 2.23 and ε = 35.94 are from SCRF calculations with the Onsager reaction field except as noted.