Activation Energy and NBO Interaction Approaches to the Determination of the Relative Resonance Acceptor Strengths of CN, NO, COMe, CHO and NO₂ Groups from the Ring-Opening of 1,2-Benzo-3-Carbomethoxycyclobutenes

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Abstract: The relative resonance-acceptor ability based on the activation energies for the outward ring-openings of 1,2-benzo-3-carbomethoxycyclobutenes bearing CN, NO, COMe, CHO and NO₂ as C6 and C7 substituents is different from that based on the $\sigma_{C3C4}^{\text{C}6} \rightarrow \sigma_{C1C2}^{\text{C}7}$ interactions in the inward opening transition structures. The differential activation energy ($\Delta G^\ddagger$) predicts outward ring-opening and, in contrast, the differential $\sigma_{C3C4}^{\text{C}6} \rightarrow \sigma_{C1C2}^{\text{C}7}$ interaction energy predicts inward opening, throughout. The relative resonance-acceptor ability estimated from the $\sigma_{C3C4}^{\text{C}6} \rightarrow \sigma_{C1C2}^{\text{C}7}$ interaction energies is more realistic than that from the activation energies.

Keywords: relative resonance-acceptor ability, 1,2-benzo-3-carbomethoxycyclobutenes, conrotatory ring-opening, torquoselectivity, transition structure, activation energy, NBO analysis

Introduction: The effect of a C1-substituent on the efficacy of the conrotatory thermal ring-opening of a given 3-substituted cyclobutene (Scheme 1) was observed by Houk to be minimal; a donor substituent raised the activation energy slightly, and a powerful acceptor substituent slightly lowered it.¹ This premise was lately used by us² as a strategic tool to estimate the relative resonance-acceptor ability of the functional groups CN, NO, COMe, CHO and NO₂ from MP2/6-31+G(d,p) level quantum chemical calculations to discover that the relative acceptor ability based on the Gibbs' free energy of activation for outward opening $\Delta G_{\text{out}}^{\ddagger}$ (CN < NO < NO₂ < COMe < CHO) was different from that based on the Gibbs' free energy of activation for inward opening $\Delta G_{\text{in}}^{\ddagger}$ (CN < NO < CHO < NO₂ < COMe). It was also discovered that the relative acceptor ability from the NBO interactions in the outward opening transition structures was much the same as that from the inward opening transition structures. The relative acceptor ability from the $\sigma_{\text{C3C4}}^{\text{C1C2}}$ NBO interactions was estimated to be CN < COMe < CHO < NO₂ < NO, which is in accordance with the text book wisdom.³

Scheme 1. Conrotatory outward (1→2) and inward (1→3) openings of 1-R-3-CO₂Me-cyclobutene (R = H, CN, NO, COMe, CHO and NO₂)

The above study was warranted primarily because (a) NO₂ and COMe were previously noted to possess, more or less, similar electron-accepting power based on the Taft σ_{R}^0 parameters and (b) CHO and NO, as C3-substituents on cyclobutene, were debated to be stronger acceptors than CN, COMe and NO₂ to align with the predicted ring-openings based on the differential energies of activation.¹ 3-CO₂Me-cyclobutene was predicted to open outward and it was considered vindicated from the experimentally observed predominantly outward opening of 1,2-benzo-3-carbomethoxycyclobutene.¹ It is to be noted that the experimental results of the ring-openings of 3-CO₂Me- and 3-NO₂-cyclobutenes are hitherto not reported. We have recently shown from the study of the NBO interactions that 1,2-benzo-3-CO₂Me-cyclobutene and 1,2-benzo-3-CONMe₂-cyclobutene opened

inward faster than outward in an equilibrium process and that the outward opened product predominated because it was significantly more stable than the inward opened variant.⁴ We have also demonstrated that unlike the four-electron process in the ring-opening of 3-substituted cyclobutenes, the ring-opening in 1,2-benzo-3-CO₂Me-cyclobutene is an eight-electron process for the absence of the $\pi_{C3C4} - \pi_{C1C2}^*$ and $\pi_{C1C2} - \pi_{C3C4}^*$ interactions.⁴

Scheme 2. Conrotatory outward (4→5 and 7→8) and inward (4→6 and 7→9) openings of 6- and 7-R-1,2-benzo-3-CO₂Me-cyclobutenes (R = H, CN, NO, COMe, CHO and NO₂)

We wondered about the effect of resonance-acceptors located on the aromatic ring in 3-CO₂Me-1,2-benzocyclobutene on the efficacy of ring-opening, with focus to explore whether (a) the acceptors lowered the energies of activation as they do for the opening of 3-CO₂Me-cyclobutenes bearing the acceptors on C1 and (b) there existed an acceptable trend in the relative acceptor strengths of the chosen functional groups from the point of view of the energy of activation and also the NBO interaction energies. We chose to study the substrates bearing the resonance acceptors on C6 and C7 (Scheme 2). Substituents on C5 and C8 are likely to introduce the element of steric effects and, hence, such substrates were excluded from the present investigation.

Computational methods: The geometry optimizations of all the structures studied herein and the transition structure searches were carried out using the quantum chemical MP2 method at the 6-31+G(d,p) level of theory.⁵ The optimized structures were verified as minima or first order saddle

points on their potential energy surfaces by harmonic vibrational frequency analysis. The Cartesian coordinates of the optimized structures and their Gibbs' free energies are given in the [Supplementary Information](#).

Results and Discussion: The Gibbs' free energies of activation and the most relevant NBO interactions in the transition structures for the inward and outward openings are collected in [Table 1](#). The absence of the $\sigma_{C1C2}^* \leftarrow \sigma_{C3C4}$ and $\sigma_{C3C4}^* \leftarrow \sigma_{C1C2}$ interactions in both the transition structures (not shown) suggests eight-electron process. Further, while a comparison of the $\sigma_{C3C4}^* \leftarrow \sigma_{CO}$ interaction energies suggests inward opening in all the instances, the differential activation energies call for outward opening. It is surprising to note that all the acceptors raised the activation energies of both the inward and outward ring-opening reactions in reference to the unsubstituted species (R = H). This is in contrast to the lowering of activation energies of the reactions of 3-CO₂Me-cyclobutenes bearing the acceptors on C1.

Table 1. Gibbs' free energies of activation and the significant NBO interactions (kcal/mol) in the TSs for inward (4→6) and outward (4→5) openings (σ_{CO} and σ_{CO}^* correspond to CO₂Me)

R	$\Delta G_{in}^\ddagger$	$\Delta G_{out}^\ddagger$	inward TS (4→6)		outward TS (4→5)	
			$\sigma_{C3C4}^* \leftarrow \sigma_{CO}$	$\sigma_{CO}^* \leftarrow \sigma_{C3C4}$	$\sigma_{C3C4}^* \leftarrow \sigma_{CO}$	$\sigma_{CO}^* \leftarrow \sigma_{C3C4}$
H	37.65	35.60	71.03	0.84	38.27	4.73
CN	38.62	36.31	67.99	0.81	36.72	4.77
NO ^a	38.90	36.52	69.17	0.76	37.73	4.67
NO ^b	38.11	35.80	67.93	0.76	36.46	4.70
COMe ^a	38.89	36.17	70.48	0.78	38.54	4.61
COMe ^b	38.57	36.53	69.61	0.79	37.22	4.74
CHO ^a	38.67	36.30	69.67	0.78	38.23	4.63
CHO ^b	37.99	35.94	68.69	0.78	36.82	4.74
NO ₂	38.59	36.27	67.71	0.79	36.76	4.75

^aTorsion angle 5-6-C/N-O = ~0.0, ^bTorsion angle 5-6-C/N-O = ~180.0. NO^a is more stable than NO^b by 0.30 kcal/mol. COMe^a is less stable than COMe^b by 0.39 kcal/mol. CHO^a is more stable than CHO^b by 0.06 kcal/mol.

For the substrates bearing NO, COMe and CHO, there are two main conformers on allowing for resonance with the benzene ring. The torsion angle 5-6-C/N-O is 0° in the conformer *a* and 180° in the conformer *b*. The two conformers differ from each other by a small margin of energy, 0.06–0.39 kcal/mol, such that both exist under rapid equilibrium under the thermal conditions of the reaction. The $\pi_{C2C3}-\pi^*_{CO}$ interaction (not shown), which was previously suggested to provide for a stabilizing interaction to the ring-opening transition structure,¹ is absent throughout. This suggests reactant-like transition structures.

The energy of activation ($\Delta G^\ddagger$) supports outward opening throughout. Taking this energy into consideration, the relative resonance-acceptor strength turns out to be $NO < CN < CHO < NO_2 < COMe < H$ for the *a* series of materials and $COMe < CN < NO_2 < CHO < NO < H$ for the *b* series of materials. Both the series are significantly different from each other, the substrate with no substituent having the lowest activation energy being the common feature. That the H is the strongest acceptor among the groups studied herein casts aspersions on the applicability of the differential activation energy to torquoselectivity prediction and also the estimation of the resonance-acceptor strength.

The less the $\sigma_{ring}-\sigma^*_{C3C4}$ interaction (not measured as such by the NBO analysis) for the larger resonance-acceptor strength of the substituent (which lowers the σ_{ring}), the lower shall be σ_{C3C4} . This, in turn, will result in lower $\sigma_{C3C4}-\sigma^*_{CO}$ interaction. Thus, the lower the $\sigma_{C3C4}-\sigma^*_{CO}$ interaction, the higher will be the resonance-acceptor strength of the substituent. Going by this premise and considering the inward ring-opening, the resonance-acceptor strength turns out to be $H < COMe < CHO < NO < CN < NO_2$ for the *a* series of materials and $H < COMe < CHO < CN < NO < NO_2$ for the *b* series of materials. Except for the interchange in the positions of NO and CN, the two series are the same. From both the series, the relative acceptor strength of the COMe, CHO and NO_2 groups is $COMe < CHO < NO_2$, which is in excellent agreement with the general text book wisdom.³ The weakest point of both the relative series is probably the exhibit that CN has better acceptor strength than both COMe and CHO, a point that is difficult for a chemist to agree with.

Table 2. Gibbs' free energies of activation and the significant NBO interactions (kcal/mol) in the TSs for inward (7→9) and outward (7→8) openings (σ_{CO} and σ^*_{CO} correspond to CO_2Me)

R	$\Delta G^\ddagger_{\text{in}}$	$\Delta G^\ddagger_{\text{out}}$	inward TS (7→9)		outward TS (7→8)	
			$\sigma_{\text{C3C4}}-\sigma^*_{\text{CO}}$	$\sigma_{\text{CO}}-\sigma^*_{\text{C3C4}}$	$\sigma_{\text{C3C4}}-\sigma^*_{\text{CO}}$	$\sigma_{\text{CO}}-\sigma^*_{\text{C3C4}}$
H	37.65	35.60	71.03	0.84	38.27	4.73
CN	37.98	36.08	66.45	0.94	35.10	5.37
NO^a	38.04	35.98	66.17	1.03	35.88	5.16
NO^b	37.34	35.27	65.23	0.98	34.93	5.09
COMe^a	37.83	36.22	67.78	0.98	36.26	5.16
COMe^b	37.74	35.38	67.97	0.94	36.76	4.85
CHO^a	37.94	36.14	67.05	1.00	36.06	5.17
CHO^b	37.43	35.08	67.89	0.95	36.05	4.92
NO_2	37.58	35.52	65.34	0.98	34.95	5.19

^aTorsion angle 5-6-C/N-O = ~0.0; ^bTorsion angle 5-6-C/N-O = ~180.0; NO^a is more stable than NO^b by 0.31 kcal/mol. COMe^a is less stable than COMe^b by 0.26 kcal/mol. CHO^a is more stable than CHO^b by 0.20 kcal/mol.

We now turn to 7-R-1,2-benzo-3- CO_2Me -cyclobutene and explore the ring-opening features in the context of activation energies and NBO interaction, as above. The relevant data for the inward and outward opening transition structures are collected in Table 2. Like 6-R-1,2-benzo-3- CO_2Me -cyclobutene, the outward opening is favored over the inward opening from the differential activation energies and the inward opening from the differential $\sigma_{\text{C3C4}}-\sigma^*_{\text{CO}}$ interactions. The relative acceptor strength from the consideration of the activation energies for outward opening is $\text{COMe} < \text{CHO} < \text{CN} < \text{NO} < \text{H} < \text{NO}_2$ for the *a* series of materials and $\text{CN} < \text{H} < \text{NO}_2 < \text{COMe} < \text{NO} < \text{CHO}$ for the *b* series materials. Other than being very different from each other, the order looks suspicious. How could H ever be a more powerful acceptor than even CN? The relative acceptor order from the NBO interactions in the inward opening transition structures is $\text{H} < \text{COMe} < \text{CHO} < \text{CN} < \text{NO} < \text{NO}_2$ for both the series of materials. This order is more sensible than the one based on the activation energy above. The H is the least powerful acceptor and NO_2 the most powerful among the groups studied herein. The

CN group here as well shows up to be a better acceptor than the COMe and CHO groups. The relative order of the acceptor strengths of the prominent groups COMe, CHO and NO₂ remains, however, unchanged from COMe < CHO < NO₂.³

Conclusion: It has been shown that the performance of the NBO approach to the prediction of the torquoselectivity of the ring-opening of 1,2-benzo-3-CO₂Me-cyclobutenes bearing substituents on the aromatic ring and also the estimation of the relative resonance-acceptor strengths of the substituents is superior to that of the activation energy approach. The relative resonance-acceptor strength of the common functional groups COMe, CHO and NO₂ estimated from the NBO approach is COMe < CHO < NO₂, which has general acceptability. Two important points, however, must be noted: (a) the present study recognizes CN as a better acceptor than COMe and CHO requires attention and (b) the relative acceptor strength estimated from the NBO study of the substituted 1,2-benzo-3-CO₂Me-cyclobutenes (COMe < CHO < CN < NO < NO₂) is different the one estimated previously² from the study of the 1-substituted-3-CO₂Me-cyclobutenes (CN < COMe < CHO < NO₂ < NO).

ASSOCIATED CONTENT

Supporting Information

Cartesian coordinates of the optimized substrates, transition structures and Gibbs' free energies ([PDF](#))

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Notes

The authors declare no competing financial interest.

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Abstract: The relative resonance-acceptor ability based on the activation energies for the outward ring-openings of 1,2-benzo-3-carbomethoxycyclobutenes bearing CN, NO, COMe, CHO and NO₂ as C6 and C7 substituents is different from that based on the $\sigma_{C3C4}-\pi^*_{C1C2}$ interactions in the inward opening transition structures. The differential activation energy ($\Delta G^\ddagger$) predicts outward ring-opening and, in contrast, the differential $\sigma_{C3C4}-\pi^*_{C1C2}$ interaction energy predicts inward opening, throughout. The relative resonance-acceptor ability estimated from the $\sigma_{C3C4}-\pi^*_{C1C2}$ interaction energies is more realistic than that from the activation energies.

Keywords: relative resonance-acceptor ability, 1,2-benzo-3-carbomethoxycyclobutenes, conrotatory ring-opening, torquoselectivity, transition structure, activation energy, NBO analysis

Introduction: The effect of a C1-substituent on the efficacy of the conrotatory thermal ring-opening of a given 3-substituted cyclobutene (Scheme 1) was observed by Houk to be minimal; a donor substituent raised the activation energy slightly, and a powerful acceptor substituent slightly lowered it.¹ This premise was lately used by us² as a strategic tool to estimate the relative resonance-acceptor ability of the functional groups CN, NO, COMe, CHO and NO₂ from MP2/6-31+G(d,p) level quantum chemical calculations to discover that the relative acceptor ability based on the Gibbs' free energy of activation for outward opening $\Delta G^\ddagger_{\text{out}}$ (CN < NO < NO₂ < COMe < CHO) was different from that based on the Gibbs' free energy of activation for inward opening $\Delta G^\ddagger_{\text{in}}$ (CN < NO < CHO < NO₂ < COMe). It was also discovered that the relative acceptor ability from the NBO interactions in the outward opening transition structures was much the same as that from the inward opening transition structures. The relative acceptor ability from the $\sigma_{\text{C3C4}}-\pi^*_{\text{C1C2}}$ NBO interactions was estimated to be CN < COMe < CHO < NO₂ < NO, which is in accordance with the text book wisdom.³

Scheme 1. Conrotatory outward (**1**→**2**) and inward (**1**→**3**) openings of 1-R-3-CO₂Me-cyclobutene (R = H, CN, NO, COMe, CHO and NO₂)

The above study was warranted primarily because (a) NO₂ and COMe were previously noted to possess, more or less, similar electron-accepting power based on the Taft σ_{R}^0 parameters and (b) CHO and NO, as C3-substituents on cyclobutene, were debated to be stronger acceptors than CN, COMe and NO₂ to align with the predicted ring-openings based on the differential energies of activation.¹ 3-CO₂Me-cyclobutene was predicted to open outward and it was considered vindicated from the experimentally observed predominantly outward opening of 1,2-benzo-3-carbomethoxycyclobutene.¹ It is to be noted that the experimental results of the ring-openings of 3-CO₂Me- and 3-NO₂-

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Scheme 2. Conrotatory outward (**4**→**5** and **7**→**8**) and inward (**4**→**6** and **7**→**9**) openings of 6- and 7-R-1,2-benzo-3-CO₂Me-cyclobutenes (R = H, CN, NO, COMe, CHO and NO₂)

We wondered about the effect of resonance-acceptors located on the aromatic ring in 3-CO₂Me-1,2-benzocyclobutene on the efficacy of ring-opening, with focus to explore whether (a) the acceptors lowered the energies of activation as they do for the opening of 3-CO₂Me-cyclobutenes bearing the acceptors on C1 and (b) there existed an acceptable trend in the relative acceptor strengths of the chosen functional groups from the point of view of the energy of activation and also the NBO interaction energies. We chose to study the substrates bearing the resonance acceptors on C6 and C7 (Scheme 2). Substituents on C5 and C8 are likely to introduce the element of steric effects and, hence, such substrates were excluded from the present investigation.

Computational methods: The geometry optimizations of all the structures studied herein and the transition structure searches were carried out using the quantum chemical MP2 method at the 6-31+G(d,p) level of theory.⁵ The optimized structures were verified as minima or first order saddle points on their potential energy surfaces by harmonic vibrational frequency analysis. The Cartesian coordinates of the optimized structures and their Gibbs' free energies are given in the [Supplementary Information](#).

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Table 1. Gibbs' free energies of activation and the significant NBO interactions (kcal/mol) in the TSs for inward (4→6) and outward (4→5) openings (π_{CO} and π^*_{CO} correspond to CO₂Me)

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COMe ^b	38.57	36.53	69.61	0.79	37.22	4.74
CHO ^a	38.67	36.30	69.67	0.78	38.23	4.63
CHO ^b	37.99	35.94	68.69	0.78	36.82	4.74

NO ₂	38.59	36.27	67.71	0.79	36.76	4.75
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^aTorsion angle 5-6-C/N-O = ~0.0, ^bTorsion angle 5-6-C/N-O = ~180.0. NO^a is more stable than NO^b by 0.30 kcal/mol. COMe^a is less stable than COMe^b by 0.39 kcal/mol. CHO^a is more stable than CHO^b by 0.06 kcal/mol.

For the substrates bearing NO, COMe and CHO, there are two main conformers on allowing for resonance with the benzene ring. The torsion angle 5-6-C/N-O is 0° in the conformer *a* and 180° in the conformer *b*. The two conformers differ from each other by a small margin of energy, 0.06–0.39 kcal/mol, such that both exist under rapid equilibrium under the thermal conditions of the reaction. The $\pi_{C2C3}-\pi^*_{CO}$ interaction (not shown), which was previously suggested to provide for a stabilizing interaction to the ring-opening transition structure,¹ is absent throughout. This suggests reactant-like transition structures.

The energy of activation ($\Delta G^\ddagger$) supports outward opening throughout. Taking this energy into consideration, the relative resonance-acceptor strength turns out to be NO < CN < CHO < NO₂ < COMe < H for the *a* series of materials and COMe < CN < NO₂ < CHO < NO < H for the *b* series of materials. Both the series are significantly different from each other, the substrate with no substituent having the lowest activation energy being the common feature. That the H is the strongest acceptor among the groups studied herein casts aspersions on the applicability of the differential activation energy to torquoselectivity prediction and also the estimation of the resonance-acceptor strength.

The less the $\pi_{ring}-\sigma^*_{C3C4}$ interaction (not measured as such by the NBO analysis) for the larger resonance-acceptor strength of the substituent (which lowers the π_{ring}), the lower shall be σ_{C3C4} . This, in turn, will result in lower $\sigma_{C3C4}-\pi^*_{CO}$ interaction. Thus, the lower the $\sigma_{C3C4}-\pi^*_{CO}$ interaction, the higher will be the resonance-acceptor strength of the substituent. Going by this premise and considering the inward ring-opening, the resonance-acceptor strength turns out to be H < COMe < CHO < NO < CN < NO₂ for the *a* series of materials and H < COMe < CHO < CN < NO < NO₂ for the *b* series of materials. Except for the interchange in the positions of NO and CN, the two series are the same. From both the series, the relative acceptor strength of the COMe, CHO and NO₂ groups is COMe < CHO < NO₂, which

is in excellent agreement with the general text book wisdom.³ The weakest point of both the relative series is probably the exhibit that CN has better acceptor strength than both COMe and CHO, a point that is difficult for a chemist to agree with.

Table 2. Gibbs' free energies of activation and the significant NBO interactions (kcal/mol) in the TSs for inward (**7**→**9**) and outward (**7**→**8**) openings (π_{CO} and π^*_{CO} correspond to CO_2Me)

R	$\Delta G^\ddagger_{\text{in}}$	$\Delta G^\ddagger_{\text{out}}$	inward TS (7 → 9)		outward TS (7 → 8)	
			$\sigma_{\text{C3C4}}-\pi^*_{\text{CO}}$	$\pi_{\text{CO}}-\sigma^*_{\text{C3C4}}$	$\sigma_{\text{C3C4}}-\pi^*_{\text{CO}}$	$\pi_{\text{CO}}-\sigma^*_{\text{C3C4}}$
H	37.65	35.60	71.03	0.84	38.27	4.73
CN	37.98	36.08	66.45	0.94	35.10	5.37
NO^a	38.04	35.98	66.17	1.03	35.88	5.16
NO^b	37.34	35.27	65.23	0.98	34.93	5.09
COMe^a	37.83	36.22	67.78	0.98	36.26	5.16
COMe^b	37.74	35.38	67.97	0.94	36.76	4.85
CHO^a	37.94	36.14	67.05	1.00	36.06	5.17
CHO^b	37.43	35.08	67.89	0.95	36.05	4.92
NO_2	37.58	35.52	65.34	0.98	34.95	5.19

^aTorsion angle 5-6-C/N-O = $\sim 0.0^\circ$; ^bTorsion angle 5-6-C/N-O = $\sim 180.0^\circ$; NO^a is more stable than NO^b by 0.31 kcal/mol. COMe^a is less stable than COMe^b by 0.26 kcal/mol. CHO^a is more stable than CHO^b by 0.20 kcal/mol.

We now turn to 7-R-1,2-benzo-3- CO_2Me -cyclobutene and explore the ring-opening features in the context of activation energies and NBO interaction, as above. The relevant data for the inward and outward opening transition structures are collected in Table 2. Like 6-R-1,2-benzo-3- CO_2Me -cyclobutene, the outward opening is favored over the inward opening from the differential activation energies and the inward opening from the differential $\sigma_{\text{C3C4}}-\pi^*_{\text{CO}}$ interactions. The relative acceptor strength from the consideration of the activation energies for outward opening is $\text{COMe} < \text{CHO} < \text{CN} <$

$\text{NO} < \text{H} < \text{NO}_2$ for the *a* series of materials and $\text{CN} < \text{H} < \text{NO}_2 < \text{COMe} < \text{NO} < \text{CHO}$ for the *b* series materials. Other than being very different from each other, the order looks suspicious. How could H ever be a more powerful acceptor than even CN? The relative acceptor order from the NBO interactions in the inward opening transition structures is $\text{H} < \text{COMe} < \text{CHO} < \text{CN} < \text{NO} < \text{NO}_2$ for both the series of materials. This order is more sensible than the one based on the activation energy above. The H is the least powerful acceptor and NO_2 the most powerful among the groups studied herein. The CN group here as well shows up to be a better acceptor than the COMe and CHO groups. The relative order of the acceptor strengths of the prominent groups COMe, CHO and NO_2 remains, however, unchanged from $\text{COMe} < \text{CHO} < \text{NO}_2$.³

Conclusion: It has been shown that the performance of the NBO approach to the prediction of the torquoselectivity of the ring-opening of 1,2-benzo-3- CO_2Me -cyclobutenes bearing substituents on the aromatic ring and also the estimation of the relative resonance-acceptor strengths of the substituents is superior to that of the activation energy approach. The relative resonance-acceptor strength of the common functional groups COMe, CHO and NO_2 estimated from the NBO approach is $\text{COMe} < \text{CHO} < \text{NO}_2$, which has general acceptability. Two important points, however, must be noted: (a) the present study recognizes CN as a better acceptor than COMe and CHO requires attention and (b) the relative acceptor strength estimated from the NBO study of the substituted 1,2-benzo-3- CO_2Me -cyclobutenes ($\text{COMe} < \text{CHO} < \text{CN} < \text{NO} < \text{NO}_2$) is different the one estimated previously² from the study of the 1-substituted-3- CO_2Me -cyclobutenes ($\text{CN} < \text{COMe} < \text{CHO} < \text{NO}_2 < \text{NO}$).

ASSOCIATED CONTENT

Supporting Information

Cartesian coordinates of the optimized substrates, transition structures and Gibbs' free energies ([PDF](#))

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Notes

The authors declare no competing financial interest.

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Supplementary Information

on

Activation energy and NBO interaction approaches to the determination of the relative resonance acceptor strengths of CN, NO, COMe, CHO and NO₂ groups from the ring-opening of 1,2-benzo-3-carbomethoxycyclobutenes

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Table of Contents

1. MP2/6-31+G(d,p) coordinates of **4**, R = H, CN, NO, COMe, CHO, NO₂
S2–S6
2. MP2/6-31+G(d,p) coordinates of the transition structures for the reactions **4**→**6** and **4**→**5**
S6–S15
3. MP2/6-31+G(d,p) coordinates of **7**, R = CN, NO, COMe, CHO, NO₂ S15–S19
4. MP2/6-31+G(d,p) coordinates of the transition structures for the reactions **7**→**9** and **7**→**8**
S19–S27

4, R=H (G=-535.797806 Hartrees)

1	6	0	-1.425556	0.937675	0.037653
2	6	0	-0.322398	1.938248	0.349680
3	6	0	0.530787	0.706851	0.817871
4	6	0	-0.665082	-0.160689	0.443078
5	1	0	-0.540779	2.655134	1.142824
6	1	0	0.108228	2.457798	-0.506105
7	1	0	0.780880	0.696470	1.882040
8	6	0	1.772526	0.424535	0.014859
9	8	0	2.266687	1.149046	-0.837475
10	6	0	-1.127339	-1.470549	0.394471
11	6	0	-2.727599	0.797824	-0.431908
12	1	0	-3.340110	1.634628	-0.747328
13	6	0	-2.438761	-1.621845	-0.087176
14	6	0	-3.215679	-0.519188	-0.489813
15	8	0	2.277939	-0.788417	0.357621
16	6	0	3.459206	-1.175746	-0.379822
17	1	0	4.252866	-0.448762	-0.224774
18	1	0	3.230876	-1.245155	-1.440811
19	1	0	3.735070	-2.144356	0.022219
20	1	0	-0.533340	-2.322129	0.704127
21	1	0	-4.221508	-0.697444	-0.851886
22	1	0	-2.869827	-2.613918	-0.154843

4, R=CN (G=-627.813836 Hartrees)

1	6	0	0.673086	1.119421	-0.177020
2	6	0	-0.534961	2.032765	-0.318630
3	6	0	-1.321533	0.760055	-0.793406
4	6	0	-0.029007	-0.017068	-0.587128
5	1	0	-0.449196	2.814966	-1.073836
6	1	0	-0.921800	2.456027	0.607955
7	1	0	-1.666455	0.792311	-1.830294
8	6	0	-2.459266	0.322186	0.092996
9	8	0	-2.962162	0.974514	0.996186
10	6	0	0.546399	-1.279076	-0.678552
11	6	0	2.020491	1.077872	0.153603
12	1	0	2.597867	1.939393	0.467294
13	6	0	1.904328	-1.348593	-0.337265
14	1	0	2.429767	-2.295014	-0.379495
15	6	0	2.620665	-0.198051	0.066909
16	8	0	-2.851204	-0.930617	-0.247435
17	6	0	-3.934939	-1.459469	0.552426
18	1	0	-4.808295	-0.817464	0.468256
19	1	0	-3.630080	-1.527568	1.593923
20	1	0	-4.132732	-2.442442	0.139914
21	1	0	-0.000223	-2.160174	-0.991604
22	6	0	4.011315	-0.338946	0.401569
23	7	0	5.158371	-0.448255	0.679266

4, R=NO^a (G=-664.786778 Hartrees, torsion angle 5-6-N-0=0.0)

1	6	0	0.684521	1.012222	-0.249258
2	6	0	-0.475771	1.980096	-0.429344
3	6	0	-1.332965	0.731263	-0.837296
4	6	0	-0.083833	-0.106408	-0.602339
5	1	0	-0.354372	2.719244	-1.222047
6	1	0	-0.831450	2.467771	0.477842
7	1	0	-1.685635	0.731155	-1.872073
8	6	0	-2.483942	0.396836	0.077031
9	8	0	-2.936897	1.113406	0.957569
10	6	0	0.413649	-1.404043	-0.630444
11	6	0	2.025909	0.918278	0.083787
12	1	0	2.661039	1.752000	0.356221
13	6	0	1.768063	-1.523997	-0.286717
14	1	0	2.263754	-2.487790	-0.274780
15	6	0	2.538032	-0.395635	0.058592
16	8	0	-2.952044	-0.843623	-0.207832
17	6	0	-4.053713	-1.275998	0.624922
18	1	0	-4.889988	-0.588712	0.523508
19	1	0	-3.739605	-1.318887	1.664997
20	1	0	-4.312682	-2.261958	0.255707
21	7	0	3.905796	-0.717261	0.376117
22	8	0	4.605757	0.264910	0.688091
23	1	0	-0.185869	-2.265214	-0.898430

4, R=NO^b (G=-664.786300 Hartrees, torsion angle 5-6-N-0=180.0)

1	6	0	-0.567633	1.235008	0.134961
2	6	0	0.686964	2.084186	0.272744
3	6	0	1.396559	0.781198	0.784063
4	6	0	0.065012	0.071803	0.581254
5	1	0	0.635937	2.885402	1.010948
6	1	0	1.106929	2.465853	-0.657403
7	1	0	1.734032	0.816853	1.823339
8	6	0	2.514317	0.258119	-0.081446
9	8	0	3.056574	0.856278	-0.999160
10	6	0	-0.574318	-1.162801	0.688133
11	6	0	-1.910739	1.246681	-0.219063
12	1	0	-2.459376	2.115014	-0.565492
13	6	0	-1.925878	-1.174863	0.327786
14	1	0	-2.511639	-2.084286	0.376761
15	6	0	-2.563717	0.004399	-0.113718
16	8	0	2.835730	-1.004114	0.296425
17	6	0	3.892472	-1.613678	-0.481937
18	1	0	4.799995	-1.019509	-0.408557
19	1	0	3.589813	-1.692076	-1.523329
20	1	0	4.032541	-2.594891	-0.042471
21	7	0	-3.954720	0.046808	-0.493025
22	8	0	-4.548828	-1.044773	-0.415847
23	1	0	-0.071232	-2.059460	1.029374

4, R=COMe^a (G=-687.994469 Hartrees, torsion angle 5-6-C-0=0.0)

1	6	0	0.205011	1.188752	-0.242481
2	6	0	-1.040005	2.057600	-0.349805
3	6	0	-1.794016	0.757356	-0.802000
4	6	0	-0.468029	0.027554	-0.633874
5	1	0	-1.006397	2.841735	-1.107346
6	1	0	-1.415378	2.467597	0.587453
7	1	0	-2.172137	0.775566	-1.827622
8	6	0	-2.884753	0.275209	0.118498
9	8	0	-3.367194	0.894278	1.055785
10	6	0	0.150511	-1.212472	-0.726514
11	6	0	1.557422	1.192712	0.062351
12	1	0	2.117530	2.070005	0.362029
13	6	0	1.519111	-1.224543	-0.413093
14	1	0	2.054647	-2.163798	-0.468428
15	6	0	2.212263	-0.055781	-0.023228
16	8	0	-3.260725	-0.981356	-0.231219
17	6	0	-4.293773	-1.552531	0.604410
18	1	0	-5.187630	-0.934457	0.568956
19	1	0	-3.943320	-1.628611	1.630987
20	1	0	-4.482551	-2.534134	0.184173
21	1	0	-0.368798	-2.115660	-1.023809
22	6	0	4.396520	-1.425511	0.299699
23	1	0	3.935220	-2.113686	1.008891
24	1	0	5.432064	-1.251942	0.579514
25	1	0	4.359964	-1.886975	-0.687935
26	6	0	3.675322	-0.095407	0.295583
27	8	0	4.285830	0.946668	0.557415

4, R=COMe^b (G=-687.995085 Hartrees, torsion angle 5-6-C-O=180.00)

1	6	0	0.240679	1.114286	-0.307669
2	6	0	-0.970848	2.023612	-0.455889
3	6	0	-1.773977	0.730860	-0.838892
4	6	0	-0.473668	-0.037295	-0.641256
5	1	0	-0.911663	2.764541	-1.254470
6	1	0	-1.328077	2.495885	0.458947
7	1	0	-2.159753	0.711614	-1.861588
8	6	0	-2.872387	0.335240	0.113446
9	8	0	-3.314087	1.013312	1.030138
10	6	0	0.102340	-1.303164	-0.684958
11	6	0	1.597123	1.082282	-0.008164
12	1	0	2.157894	1.973072	0.246873
13	6	0	1.467744	-1.350140	-0.377571
14	1	0	2.002148	-2.292089	-0.386189
15	6	0	2.206375	-0.191264	-0.044802
16	8	0	-3.305391	-0.916822	-0.178203
17	6	0	-4.346085	-1.411539	0.695935
18	1	0	-5.215004	-0.759625	0.648902
19	1	0	-3.981059	-1.460366	1.719059
20	1	0	-4.580681	-2.400831	0.319194
21	1	0	-0.451616	-2.199083	-0.938556
22	6	0	4.472986	0.844678	0.668563
23	1	0	4.471016	1.590907	-0.126986

24	1	0	5.493137	0.525347	0.863778
25	1	0	4.057037	1.308094	1.564026
26	6	0	3.661325	-0.367286	0.267205
27	8	0	4.191601	-1.481377	0.201980

4, R=CHO^a (G=-648.828009 Hartrees, torsion angle 5-6-C-O=0.0)

1	6	0	0.658495	1.014961	-0.248779
2	6	0	-0.505075	1.979058	-0.428202
3	6	0	-1.359602	0.725912	-0.830897
4	6	0	-0.106711	-0.105877	-0.591826
5	1	0	-0.388322	2.716441	-1.223398
6	1	0	-0.861212	2.468647	0.477811
7	1	0	-1.709867	0.720594	-1.866515
8	6	0	-2.511675	0.392641	0.081359
9	8	0	-2.969381	1.109943	0.959119
10	6	0	0.400121	-1.399203	-0.628324
11	6	0	2.005698	0.921412	0.064560
12	1	0	2.640749	1.759987	0.325373
13	6	0	1.758796	-1.510937	-0.294976
14	1	0	2.234075	-2.486994	-0.294292
15	6	0	2.540944	-0.383987	0.035718
16	8	0	-2.977339	-0.850484	-0.200239
17	6	0	-4.079355	-1.281467	0.631875
18	1	0	-4.916869	-0.596110	0.527051
19	1	0	-3.767461	-1.320408	1.672847
20	1	0	-4.336405	-2.269207	0.265844
21	1	0	-0.196447	-2.264695	-0.889852
22	6	0	3.963764	-0.601629	0.379951
23	8	0	4.747311	0.292882	0.696640
24	1	0	4.304630	-1.652271	0.338216

4, R=CHO^b (G=-648.827913 Hartrees, torsion angle 5-6-C-O=180.0)

1	6	0	0.544636	1.227422	-0.140756
2	6	0	-0.709798	2.076433	-0.282378
3	6	0	-1.420738	0.770080	-0.783115
4	6	0	-0.088683	0.061450	-0.576713
5	1	0	-0.659812	2.871452	-1.027618
6	1	0	-1.129839	2.466148	0.644501
7	1	0	-1.759401	0.798118	-1.822179
8	6	0	-2.537077	0.254909	0.088175
9	8	0	-3.065311	0.852736	1.014718
10	6	0	0.556317	-1.168072	-0.688374
11	6	0	1.892206	1.244837	0.197045
12	1	0	2.418038	2.134392	0.530225
13	6	0	1.911283	-1.167765	-0.336099
14	1	0	2.499118	-2.076727	-0.386615
15	6	0	2.563683	0.009822	0.091953
16	8	0	-2.875563	-1.002030	-0.293235
17	6	0	-3.928758	-1.605639	0.493731
18	1	0	-4.830868	-1.001489	0.436137
19	1	0	-3.614298	-1.694937	1.530800
20	1	0	-4.084909	-2.582239	0.049352

21	1	0	0.056955	-2.069488	-1.022606
22	6	0	3.996856	-0.046786	0.459284
23	8	0	4.689615	-1.063116	0.421789
24	1	0	4.435527	0.913903	0.785307

4, R=NO₂ (G=-739.816649 Hartrees)

1	6	0	0.273609	1.162216	-0.200652
2	6	0	-0.949552	2.061952	-0.285673
3	6	0	-1.729251	0.794118	-0.783192
4	6	0	-0.421988	0.029397	-0.631491
5	1	0	-0.890966	2.869419	-1.016342
6	1	0	-1.319321	2.448957	0.663397
7	1	0	-2.100280	0.854326	-1.809642
8	6	0	-2.837968	0.310597	0.116652
9	8	0	-3.323217	0.923779	1.056146
10	6	0	0.167882	-1.222860	-0.759970
11	6	0	1.626886	1.134093	0.110964
12	1	0	2.209549	1.985500	0.435282
13	6	0	1.531693	-1.287026	-0.438781
14	1	0	2.079221	-2.217228	-0.501269
15	6	0	2.211902	-0.133608	-0.018739
16	8	0	-3.224699	-0.933604	-0.259034
17	6	0	-4.280119	-1.504840	0.549912
18	1	0	-5.163118	-0.871745	0.511741
19	1	0	-3.946361	-1.605674	1.579789
20	1	0	-4.476838	-2.475038	0.107767
21	7	0	3.644234	-0.264706	0.295584
22	8	0	4.320256	0.780541	0.335650
23	8	0	4.091393	-1.407870	0.504373
24	1	0	-0.369954	-2.102577	-1.091072

TS for 4→6, R=H (G=-535.737807 Hartrees)

1	6	0	-1.032551	0.809732	0.414758
2	6	0	-0.018747	1.428833	1.201033
3	6	0	0.568138	-0.783755	0.759996
4	6	0	-0.822517	-0.593204	0.489417
5	1	0	0.132167	1.062813	2.206841
6	1	0	0.367596	2.422984	0.983954
7	1	0	0.936231	-1.597377	1.383373
8	6	0	1.579571	-0.220343	-0.166193
9	8	0	1.386032	0.264526	-1.274927
10	6	0	-1.867020	-1.494360	0.221581
11	6	0	-2.134705	1.329113	-0.292777
12	1	0	-2.258445	2.393062	-0.459375
13	6	0	-3.011835	-0.963600	-0.368319
14	6	0	-3.126974	0.421224	-0.648920
15	8	0	2.828207	-0.409654	0.359531
16	6	0	3.900535	0.041472	-0.493029
17	1	0	3.820191	1.112784	-0.665760
18	1	0	3.871813	-0.480759	-1.446725
19	1	0	4.808895	-0.194256	0.051319

20	1	0	-1.750200	-2.563836	0.357643
21	1	0	-4.022923	0.779404	-1.142275
22	1	0	-3.822616	-1.624470	-0.651114

TS for 4→5, R=H (G=-535.741067 Hartrees)

1	6	0	1.569238	1.010525	0.081588
2	6	0	0.734839	2.109064	0.455630
3	6	0	-0.577058	0.448896	-0.417505
4	6	0	0.711885	-0.104331	-0.104181
5	1	0	0.973678	3.143093	0.212305
6	1	0	0.062225	1.962636	1.289620
7	1	0	-0.644757	1.142757	-1.244722
8	6	0	-1.830438	-0.192860	0.012371
9	8	0	-1.901779	-1.195254	0.719784
10	6	0	1.208853	-1.417170	-0.051642
11	6	0	2.963193	0.872225	-0.065529
12	1	0	3.631884	1.724885	-0.027962
13	6	0	2.596144	-1.555411	-0.073828
14	6	0	3.455133	-0.430410	-0.111643
15	8	0	-2.916916	0.471429	-0.465234
16	6	0	-4.183417	-0.092918	-0.061178
17	1	0	-4.261152	-0.102181	1.023749
18	1	0	-4.279905	-1.107788	-0.440171
19	1	0	-4.932073	0.557919	-0.499334
20	1	0	0.551493	-2.276801	-0.083184
21	1	0	4.525573	-0.592333	-0.162970
22	1	0	3.032363	-2.547250	-0.088229

TS for 4→6, R=CN (G=-627.752286 Hartrees)

1	6	0	0.401798	-0.321849	0.866062
2	6	0	-0.639991	-0.735183	1.742242
3	6	0	-1.367851	1.051830	0.415501
4	6	0	0.055578	0.965726	0.373930
5	1	0	-0.959559	-0.037116	2.503229
6	1	0	-0.897795	-1.780456	1.897962
7	1	0	-1.892206	1.981615	0.630547
8	6	0	-2.184546	0.035631	-0.299772
9	8	0	-1.786581	-0.792783	-1.109171
10	6	0	1.041182	1.839185	-0.117966
11	6	0	1.622925	-0.919127	0.504713
12	1	0	1.873040	-1.941856	0.761696
13	6	0	2.296506	1.295649	-0.363429
14	1	0	3.078910	1.900559	-0.804765
15	6	0	2.566454	-0.075487	-0.086625
16	8	0	-3.500908	0.224213	0.001775
17	6	0	-4.400602	-0.663119	-0.697928
18	1	0	-4.187876	-1.697125	-0.435334
19	1	0	-4.297790	-0.533350	-1.772701
20	1	0	-5.391589	-0.375277	-0.364145
21	1	0	0.813847	2.859999	-0.403684
22	6	0	3.868863	-0.592815	-0.407238
23	7	0	4.942719	-1.015868	-0.675796

TS for **4→5**, R=CN (G=-627.755980 Hartrees)

1	6	0	0.816825	1.163297	0.116079
2	6	0	-0.081550	2.215564	0.467277
3	6	0	-1.282168	0.466124	-0.414817
4	6	0	0.029218	-0.002106	-0.071341
5	1	0	0.101703	3.259076	0.219527
6	1	0	-0.761800	2.031644	1.287577
7	1	0	-1.374672	1.156609	-1.242708
8	6	0	-2.502071	-0.253614	-0.002658
9	8	0	-2.512164	-1.263324	0.696909
10	6	0	0.597805	-1.284297	0.018531
11	6	0	2.215504	1.108823	-0.017488
12	1	0	2.842691	1.992401	0.011747
13	6	0	1.987447	-1.351988	0.014093
14	1	0	2.487420	-2.312717	0.021091
15	6	0	2.779520	-0.171368	-0.037357
16	8	0	-3.617080	0.343782	-0.491189
17	6	0	-4.854570	-0.301427	-0.112067
18	1	0	-4.947014	-0.324660	0.971266
19	1	0	-4.880849	-1.316155	-0.501990
20	1	0	-5.633724	0.307011	-0.557209
21	1	0	-0.008830	-2.180471	-0.000945
22	6	0	4.209569	-0.307423	-0.095525
23	7	0	5.387978	-0.420845	-0.148925

TS for **4→6**, R=NO^a (G=-664.724785 Hartrees)

1	6	0	0.402188	-0.279401	0.809197
2	6	0	-0.603437	-0.753962	1.697213
3	6	0	-1.417653	1.058493	0.441986
4	6	0	0.004852	1.017172	0.370458
5	1	0	-0.926385	-0.091008	2.487727
6	1	0	-0.823384	-1.811690	1.824175
7	1	0	-1.964650	1.965650	0.693592
8	6	0	-2.220591	0.034885	-0.278367
9	8	0	-1.820192	-0.751884	-1.127058
10	6	0	0.952865	1.945436	-0.097819
11	6	0	1.632007	-0.825620	0.408280
12	1	0	1.933355	-1.845287	0.617258
13	6	0	2.217953	1.446056	-0.383451
14	1	0	2.987800	2.073314	-0.816803
15	6	0	2.526898	0.080141	-0.159229
16	8	0	-3.532687	0.165902	0.069959
17	6	0	-4.422314	-0.730294	-0.631203
18	1	0	-4.166555	-1.763888	-0.408289
19	1	0	-4.356862	-0.563814	-1.703860
20	1	0	-5.411973	-0.487985	-0.259427
21	7	0	3.868836	-0.281474	-0.564293
22	8	0	4.168533	-1.467821	-0.343975
23	1	0	0.684965	2.968008	-0.338112

TS for **4→5**, R=NO^a (G=-664.728586 Hartrees)

1	6	0	0.818117	1.060459	0.124476
2	6	0	-0.025507	2.149736	0.499201
3	6	0	-1.315309	0.463900	-0.403337
4	6	0	-0.028326	-0.067722	-0.067769
5	1	0	0.206972	3.186484	0.264855
6	1	0	-0.709027	1.986378	1.321237
7	1	0	-1.374465	1.177399	-1.214671
8	6	0	-2.569338	-0.203590	-0.005685
9	8	0	-2.630806	-1.224709	0.673984
10	6	0	0.474274	-1.378562	0.018673
11	6	0	2.209825	0.944591	-0.014350
12	1	0	2.890523	1.787174	0.018910
13	6	0	1.859820	-1.505815	0.008238
14	1	0	2.335155	-2.479533	0.005503
15	6	0	2.696432	-0.363873	-0.039886
16	8	0	-3.652752	0.457837	-0.483360
17	6	0	-4.921184	-0.132322	-0.117247
18	1	0	-5.016283	-0.171690	0.965397
19	1	0	-4.997335	-1.136858	-0.526567
20	1	0	-5.668564	0.522480	-0.550936
21	7	0	4.106111	-0.682132	-0.102991
22	8	0	4.855469	0.309898	-0.137349
23	1	0	-0.177864	-2.241933	-0.002877

TS for 4→6, R=NO^b (G=-664.725565 Hartrees)

1	6	0	0.305893	-0.549090	0.803924
2	6	0	-0.771130	-1.043233	1.593793
3	6	0	-1.383613	0.966629	0.590987
4	6	0	0.034022	0.818503	0.533727
5	1	0	-1.052501	-0.473358	2.468273
6	1	0	-1.096329	-2.080965	1.562247
7	1	0	-1.863092	1.872491	0.958884
8	6	0	-2.246129	0.130830	-0.286968
9	8	0	-1.885462	-0.572374	-1.222188
10	6	0	1.069682	1.715801	0.199994
11	6	0	1.503775	-1.132614	0.353440
12	1	0	1.724550	-2.192001	0.422738
13	6	0	2.300054	1.163847	-0.125696
14	1	0	3.124337	1.782186	-0.456763
15	6	0	2.488135	-0.243533	-0.072328
16	8	0	-3.553616	0.339767	0.039454
17	6	0	-4.492618	-0.366505	-0.800672
18	1	0	-4.340256	-1.440142	-0.714254
19	1	0	-4.370504	-0.065257	-1.838404
20	1	0	-5.470029	-0.083086	-0.425610
21	7	0	3.725109	-0.885662	-0.443658
22	8	0	4.630392	-0.100344	-0.780350
23	1	0	0.889118	2.779558	0.091965

TS for 4→5, R=NO^b (G=-664.729242 Hartrees)

1	6	0	0.718030	1.268214	0.103522
2	6	0	-0.232001	2.275009	0.456719
3	6	0	-1.345374	0.477551	-0.413924
4	6	0	-0.013304	0.066487	-0.078287
5	1	0	-0.107958	3.324542	0.197335
6	1	0	-0.890635	2.064327	1.288186
7	1	0	-1.472300	1.162508	-1.242021
8	6	0	-2.532167	-0.294646	0.001773
9	8	0	-2.496795	-1.304773	0.699475
10	6	0	0.613131	-1.193769	0.010690
11	6	0	2.117232	1.270579	-0.033825
12	1	0	2.727303	2.167004	-0.012847
13	6	0	2.001812	-1.203025	0.002103
14	1	0	2.556212	-2.132639	0.005655
15	6	0	2.726877	0.015871	-0.047796
16	8	0	-3.673598	0.256645	-0.480327
17	6	0	-4.881196	-0.439921	-0.095833
18	1	0	-4.966676	-0.468996	0.987936
19	1	0	-4.867682	-1.454160	-0.487684
20	1	0	-5.687313	0.136549	-0.535475
21	7	0	4.166114	0.075052	-0.110335
22	8	0	4.728773	-1.035127	-0.075843
23	1	0	0.040952	-2.112559	-0.006024

TS for 4→6, R=COMe^a (G=-687.932490 Hartrees)

1	6	0	-0.036197	-0.427659	0.858549
2	6	0	-1.103623	-1.014059	1.596036
3	6	0	-1.819980	0.979231	0.594844
4	6	0	-0.394359	0.922722	0.597208
5	1	0	-1.467868	-0.477901	2.461323
6	1	0	-1.339717	-2.074905	1.544475
7	1	0	-2.373285	1.844254	0.957283
8	6	0	-2.587348	0.100737	-0.324529
9	8	0	-2.147356	-0.547228	-1.266395
10	6	0	0.593662	1.881795	0.317834
11	6	0	1.213602	-0.926190	0.455144
12	1	0	1.485400	-1.972645	0.530934
13	6	0	1.869934	1.403828	0.036105
14	1	0	2.640411	2.110186	-0.245326
15	6	0	2.171814	0.013019	0.069891
16	8	0	-3.918380	0.196586	-0.034392
17	6	0	-4.770653	-0.561243	-0.919233
18	1	0	-4.536930	-1.621558	-0.850328
19	1	0	-4.640600	-0.228182	-1.946368
20	1	0	-5.779232	-0.364753	-0.571637
21	1	0	0.358637	2.935427	0.214456
22	6	0	4.504276	0.440693	-0.982314
23	1	0	4.052326	0.873173	-1.875526
24	1	0	5.393768	-0.122196	-1.252316
25	1	0	4.785697	1.259778	-0.318681
26	6	0	3.538270	-0.493759	-0.289729
27	8	0	3.858861	-1.658779	-0.037604

TS for 4→5, R=COMe^a (G=-687.936829 Hartrees)

1	6	0	0.340640	1.225724	0.109583
2	6	0	-0.589140	2.256009	0.448253
3	6	0	-1.737169	0.462760	-0.418603
4	6	0	-0.414394	0.036704	-0.064784
5	1	0	-0.433316	3.302020	0.191387
6	1	0	-1.263521	2.062968	1.271503
7	1	0	-1.846762	1.142163	-1.253423
8	6	0	-2.938738	-0.283842	-0.003911
9	8	0	-2.929482	-1.284933	0.708113
10	6	0	0.195787	-1.223331	0.046299
11	6	0	1.739389	1.208837	-0.013080
12	1	0	2.347152	2.106150	0.003102
13	6	0	1.588785	-1.241300	0.055044
14	1	0	2.094126	-2.198076	0.083876
15	6	0	2.356170	-0.045743	-0.008529
16	8	0	-4.068282	0.278728	-0.504977
17	6	0	-5.289119	-0.392753	-0.120941
18	1	0	-5.385561	-0.403530	0.962347
19	1	0	-5.288511	-1.413482	-0.496141
20	1	0	-6.082657	0.188644	-0.576999
21	1	0	-0.380495	-2.139763	0.035554
22	6	0	4.553033	-1.424807	-0.132838
23	1	0	4.335183	-2.020075	0.754938
24	1	0	5.623799	-1.251672	-0.198575
25	1	0	4.217223	-1.988122	-1.004248
26	6	0	3.856209	-0.084829	-0.060116
27	8	0	4.509592	0.962730	-0.052084

TS for 4→6, R=COMe^b (G=-687.933620 Hartrees)

1	6	0	-0.003003	-0.220413	0.906604
2	6	0	-1.047080	-0.686784	1.756058
3	6	0	-1.828049	1.061869	0.428323
4	6	0	-0.400761	1.049446	0.412660
5	1	0	-1.409211	-0.014408	2.521139
6	1	0	-1.261727	-1.744437	1.897098
7	1	0	-2.404322	1.961561	0.638890
8	6	0	-2.577585	0.014089	-0.311478
9	8	0	-2.125075	-0.794021	-1.113386
10	6	0	0.556809	1.969376	-0.052165
11	6	0	1.254543	-0.754661	0.570933
12	1	0	1.521609	-1.769782	0.839759
13	6	0	1.840036	1.482099	-0.263726
14	1	0	2.611114	2.118040	-0.679851
15	6	0	2.181691	0.127966	0.011052
16	8	0	-3.910572	0.141224	-0.044265
17	6	0	-4.748874	-0.782624	-0.770306
18	1	0	-4.500044	-1.807327	-0.502425
19	1	0	-4.620396	-0.647344	-1.841742
20	1	0	-5.761282	-0.539073	-0.466405

21	1	0	0.288286	2.978896	-0.343284
22	6	0	3.917139	-1.783157	-0.225643
23	1	0	3.844208	-2.134602	0.804704
24	1	0	4.935525	-1.920886	-0.578882
25	1	0	3.230854	-2.374606	-0.832188
26	6	0	3.578470	-0.311631	-0.308285
27	8	0	4.433819	0.515362	-0.639972

TS for 4→5, R=COMe^b (G=-687.936871 Hartrees)

1	6	0	0.373618	1.156010	0.145884
2	6	0	-0.527243	2.203759	0.510991
3	6	0	-1.724259	0.479643	-0.403903
4	6	0	-0.415785	-0.002093	-0.065124
5	1	0	-0.342544	3.251425	0.279661
6	1	0	-1.205694	2.011345	1.330887
7	1	0	-1.811871	1.179893	-1.224018
8	6	0	-2.950142	-0.236903	-0.006822
9	8	0	-2.975115	-1.245915	0.693166
10	6	0	0.154978	-1.285581	0.006293
11	6	0	1.773780	1.098711	0.023930
12	1	0	2.378249	1.996571	0.077094
13	6	0	1.543856	-1.347476	0.011907
14	1	0	2.052094	-2.303411	0.004770
15	6	0	2.349518	-0.176325	-0.008584
16	8	0	-4.059407	0.365404	-0.507771
17	6	0	-5.301750	-0.275370	-0.140341
18	1	0	-5.405773	-0.297374	0.942082
19	1	0	-5.327931	-1.290776	-0.528786
20	1	0	-6.075120	0.334477	-0.593901
21	1	0	-0.450648	-2.181995	-0.035658
22	6	0	4.719219	0.866939	-0.169987
23	1	0	4.445830	1.470141	-1.036155
24	1	0	5.750607	0.537715	-0.263155
25	1	0	4.618128	1.490189	0.719734
26	6	0	3.836218	-0.356968	-0.063636
27	8	0	4.332349	-1.487524	-0.024920

TS for 4→6, R=CHO^a (G=-648.766385 Hartrees)

1	6	0	0.381169	-0.266023	0.818795
2	6	0	-0.625864	-0.747018	1.701545
3	6	0	-1.449103	1.054269	0.441064
4	6	0	-0.025016	1.023906	0.374031
5	1	0	-0.959114	-0.085479	2.489002
6	1	0	-0.835816	-1.806499	1.831581
7	1	0	-2.004515	1.956523	0.692275
8	6	0	-2.240832	0.026634	-0.283843
9	8	0	-1.832627	-0.755509	-1.133340
10	6	0	0.917730	1.953036	-0.099941
11	6	0	1.619166	-0.799748	0.422819
12	1	0	1.924114	-1.818496	0.634668
13	6	0	2.189062	1.460315	-0.374705

14	1	0	2.939577	2.115204	-0.805396
15	6	0	2.521884	0.097697	-0.147600
16	8	0	-3.556193	0.145727	0.060419
17	6	0	-4.434681	-0.757759	-0.644445
18	1	0	-4.169519	-1.789308	-0.422803
19	1	0	-4.368294	-0.589217	-1.716791
20	1	0	-5.427881	-0.526099	-0.275098
21	1	0	0.644149	2.972106	-0.349681
22	6	0	3.884209	-0.363071	-0.514117
23	8	0	4.300985	-1.505672	-0.334876
24	1	0	4.533631	0.401475	-0.976994

TS for 4→5, R=CHO^a (G=-648.770160 Hartrees)

1	6	0	0.791665	1.063185	0.126770
2	6	0	-0.057519	2.149432	0.497325
3	6	0	-1.338767	0.462937	-0.406767
4	6	0	-0.049717	-0.065750	-0.069582
5	1	0	0.173120	3.187248	0.265369
6	1	0	-0.743100	1.984423	1.317366
7	1	0	-1.400379	1.171338	-1.222255
8	6	0	-2.590557	-0.205708	-0.006260
9	8	0	-2.650992	-1.223826	0.678415
10	6	0	0.460040	-1.372985	0.011828
11	6	0	2.184690	0.947072	-0.009699
12	1	0	2.860613	1.794589	0.019218
13	6	0	1.847354	-1.492545	0.009090
14	1	0	2.301649	-2.478175	0.011562
15	6	0	2.693095	-0.353813	-0.035559
16	8	0	-3.676768	0.450447	-0.487126
17	6	0	-4.942785	-0.141442	-0.117350
18	1	0	-5.037927	-0.174908	0.965545
19	1	0	-5.016241	-1.148725	-0.520519
20	1	0	-5.692601	0.508283	-0.554644
21	1	0	-0.186820	-2.240468	-0.015288
22	6	0	4.159646	-0.568895	-0.095377
23	8	0	4.992279	0.334978	-0.140325
24	1	0	4.482670	-1.625336	-0.100592

TS for 4→6, R=CHO^b (G=-648.767378 Hartrees)

1	6	0	0.287226	-0.511188	0.831392
2	6	0	-0.788849	-0.992561	1.630098
3	6	0	-1.414930	0.982917	0.564087
4	6	0	0.004963	0.845681	0.520522
5	1	0	-1.082619	-0.399393	2.484752
6	1	0	-1.100094	-2.035287	1.631051
7	1	0	-1.905255	1.894127	0.903409
8	6	0	-2.262231	0.115664	-0.295899
9	8	0	-1.889293	-0.614133	-1.206126
10	6	0	1.035370	1.737787	0.165382
11	6	0	1.492670	-1.097114	0.403253
12	1	0	1.693341	-2.158614	0.515039

13	6	0	2.270246	1.179171	-0.136127
14	1	0	3.092049	1.795288	-0.480201
15	6	0	2.482480	-0.224043	-0.048457
16	8	0	-3.575414	0.325596	0.010383
17	6	0	-4.500196	-0.412771	-0.816813
18	1	0	-4.341890	-1.482264	-0.695653
19	1	0	-4.369339	-0.143404	-1.862283
20	1	0	-5.483660	-0.124924	-0.461223
21	1	0	0.850517	2.796761	0.023006
22	6	0	3.797031	-0.788947	-0.431981
23	8	0	4.758714	-0.119026	-0.804878
24	1	0	3.872221	-1.889369	-0.365682

TS for 4→5, R=CHO^b (G=-648.770639 Hartrees)

1	6	0	0.695460	1.265735	0.106733
2	6	0	-0.254273	2.274245	0.455710
3	6	0	-1.368139	0.473917	-0.414644
4	6	0	-0.035805	0.064054	-0.075035
5	1	0	-0.125367	3.324178	0.199244
6	1	0	-0.917462	2.065235	1.283977
7	1	0	-1.494253	1.153374	-1.247238
8	6	0	-2.555230	-0.294932	0.003855
9	8	0	-2.524492	-1.293929	0.717783
10	6	0	0.592477	-1.192716	0.017981
11	6	0	2.095707	1.267293	-0.026354
12	1	0	2.680671	2.182335	-0.003004
13	6	0	1.982434	-1.194041	0.013160
14	1	0	2.537105	-2.124513	0.021542
15	6	0	2.720806	0.017963	-0.038314
16	8	0	-3.695500	0.245866	-0.495574
17	6	0	-4.903134	-0.448659	-0.109227
18	1	0	-4.997464	-0.460492	0.974196
19	1	0	-4.883200	-1.469297	-0.483965
20	1	0	-5.708119	0.117284	-0.564548
21	1	0	0.024407	-2.114090	0.001017
22	6	0	4.199686	-0.026727	-0.101808
23	8	0	4.865894	-1.060677	-0.099191
24	1	0	4.696537	0.959126	-0.157715

TS for 4→6, R=NO₂ (G=-739.755158 Hartrees)

1	6	0	0.021415	-0.396097	0.854604
2	6	0	-1.027091	-0.965678	1.628038
3	6	0	-1.770939	0.994211	0.576477
4	6	0	-0.345872	0.944921	0.560807
5	1	0	-1.384184	-0.400887	2.477727
6	1	0	-1.257305	-2.028562	1.614244
7	1	0	-2.323719	1.867311	0.919414
8	6	0	-2.545659	0.081364	-0.306783
9	8	0	-2.108564	-0.596224	-1.228336
10	6	0	0.630341	1.903856	0.237016
11	6	0	1.266898	-0.906677	0.442788
12	1	0	1.553144	-1.944864	0.545636

13	6	0	1.904678	1.434434	-0.061055
14	1	0	2.685774	2.102603	-0.394659
15	6	0	2.176468	0.049127	0.017727
16	8	0	-3.871236	0.184747	-0.007273
17	6	0	-4.732833	-0.603808	-0.857618
18	1	0	-4.494792	-1.660401	-0.756416
19	1	0	-4.614968	-0.302971	-1.895924
20	1	0	-5.737261	-0.397848	-0.504158
21	7	0	3.527457	-0.403661	-0.363072
22	8	0	3.864101	-1.555867	-0.036695
23	8	0	4.244347	0.395387	-0.993880
24	1	0	0.387490	2.952987	0.113111

TS for 4→5, R=NO₂ (G=-739.758856 Hartrees)

1	6	0	0.404043	1.187844	0.180794
2	6	0	-0.503939	2.210735	0.586949
3	6	0	-1.685718	0.494960	-0.391126
4	6	0	-0.370545	0.025192	-0.067373
5	1	0	-0.328254	3.267653	0.398539
6	1	0	-1.187513	1.974802	1.390925
7	1	0	-1.784172	1.229173	-1.179699
8	6	0	-2.898889	-0.258648	-0.019529
9	8	0	-2.897210	-1.306182	0.621789
10	6	0	0.212815	-1.253668	-0.039794
11	6	0	1.805163	1.158780	0.051115
12	1	0	2.434350	2.036455	0.119209
13	6	0	1.603644	-1.309792	-0.035602
14	1	0	2.127123	-2.254785	-0.071785
15	6	0	2.353900	-0.113801	-0.026520
16	8	0	-4.019230	0.353957	-0.474045
17	6	0	-5.250650	-0.323624	-0.132472
18	1	0	-5.342313	-0.409237	0.947756
19	1	0	-5.267163	-1.314619	-0.579684
20	1	0	-6.035528	0.301840	-0.542452
21	7	0	3.821965	-0.228284	-0.081112
22	8	0	4.465571	0.782307	-0.417147
23	8	0	4.325080	-1.328435	0.214079
24	1	0	-0.382906	-2.154336	-0.111063

7, R=CN (G=-627.813754 Hartrees)

1	6	0	0.440030	-1.659258	0.019340
2	6	0	-0.957358	-2.193626	0.292990
3	6	0	-1.305668	-0.750157	0.801928
4	6	0	0.129334	-0.371481	0.462971
5	1	0	-1.026995	-2.967057	1.059123
6	1	0	-1.534516	-2.490635	-0.582457
7	1	0	-1.548445	-0.681929	1.865500
8	6	0	-2.346292	-0.004211	0.006406
9	8	0	-3.092170	-0.484986	-0.834215
10	6	0	1.034943	0.678532	0.466702
11	6	0	1.710717	-1.993831	-0.437940
12	1	0	1.979089	-2.985832	-0.781389

13	6	0	2.323106	0.345601	-0.005529
14	6	0	2.653497	-0.955416	-0.449951
15	8	0	-2.332090	1.307153	0.348946
16	6	0	-3.283085	2.127994	-0.369604
17	1	0	-4.293563	1.766305	-0.196058
18	1	0	-3.063883	2.105495	-1.434327
19	1	0	-3.151353	3.125700	0.033648
20	1	0	0.800690	1.681214	0.802607
21	6	0	3.336442	1.364563	-0.045969
22	7	0	4.165322	2.211014	-0.076028
23	1	0	3.661802	-1.139954	-0.800363

7, R=NO^a (G=-664.786279 Hartrees)

1	6	0	-0.425207	1.593724	0.033601
2	6	0	0.952041	2.194460	0.267260
3	6	0	1.377481	0.777253	0.789842
4	6	0	-0.045843	0.327965	0.486817
5	1	0	1.003462	2.983412	1.019012
6	1	0	1.494344	2.502770	-0.626467
7	1	0	1.644945	0.736579	1.848765
8	6	0	2.432760	0.067032	-0.018432
9	8	0	3.121870	0.562166	-0.898481
10	6	0	-0.909018	-0.757944	0.517223
11	6	0	-1.720141	1.868385	-0.408633
12	1	0	-2.030934	2.845774	-0.758773
13	6	0	-2.211122	-0.478332	0.064470
14	6	0	-2.617463	0.794722	-0.389007
15	8	0	2.503413	-1.232252	0.360855
16	6	0	3.470911	-2.021728	-0.370360
17	1	0	4.466194	-1.602869	-0.243703
18	1	0	3.213387	-2.040694	-1.426553
19	1	0	3.406964	-3.013255	0.063428
20	1	0	-0.647671	-1.753627	0.855554
21	7	0	-3.097214	-1.616653	0.103849
22	8	0	-4.257156	-1.386165	-0.284314
23	1	0	-3.641607	0.915267	-0.719371

7, R=NO^b (G=-664.786771 Hartrees)

1	6	0	0.457862	-1.704045	0.048753
2	6	0	-0.934235	-2.232221	0.357043
3	6	0	-1.284387	-0.775446	0.821496
4	6	0	0.144848	-0.397990	0.450750
5	1	0	-0.991841	-2.981340	1.148001
6	1	0	-1.518368	-2.559985	-0.502800
7	1	0	-1.512863	-0.670856	1.885036
8	6	0	-2.336224	-0.061501	0.011931
9	8	0	-3.058625	-0.565431	-0.835899
10	6	0	1.037783	0.658250	0.406027
11	6	0	1.720824	-2.053506	-0.418103
12	1	0	1.985825	-3.057080	-0.728580
13	6	0	2.313126	0.301185	-0.076719
14	6	0	2.652574	-1.006054	-0.476608

15	8	0	-2.358353	1.251568	0.345851
16	6	0	-3.312800	2.046558	-0.396462
17	1	0	-4.318754	1.665934	-0.237619
18	1	0	-3.074206	2.019496	-1.456922
19	1	0	-3.208208	3.050101	0.000200
20	1	0	0.815352	1.674076	0.707015
21	7	0	3.400049	1.238208	-0.209058
22	8	0	3.117366	2.402882	0.128983
23	1	0	3.663393	-1.171313	-0.831059

7, R=COMe^a (G=-687.994348 Hartrees)

1	6	0	-0.080621	1.807587	-0.062529
2	6	0	-1.521452	2.213758	-0.330829
3	6	0	-1.751198	0.734817	-0.802878
4	6	0	-0.281847	0.488383	-0.478525
5	1	0	-1.664608	2.959335	-1.114479
6	1	0	-2.112715	2.481753	0.544687
7	1	0	-2.003817	0.618400	-1.859661
8	6	0	-2.701947	-0.081915	0.032811
9	8	0	-3.408736	0.334967	0.939593
10	6	0	0.710544	-0.477395	-0.476900
11	6	0	1.164882	2.256511	0.361000
12	1	0	1.354566	3.273833	0.683287
13	6	0	1.978828	-0.038785	-0.039077
14	6	0	2.189302	1.295438	0.377025
15	8	0	-2.646683	-1.381419	-0.348634
16	6	0	-3.485763	-2.272308	0.422116
17	1	0	-4.526984	-1.970190	0.339138
18	1	0	-3.182845	-2.258095	1.466360
19	1	0	-3.327825	-3.251929	-0.014819
20	1	0	0.567851	-1.504418	-0.788956
21	6	0	3.087638	-1.045641	-0.001657
22	1	0	3.175041	1.596462	0.708387
23	8	0	2.861087	-2.232564	-0.259635
24	6	0	4.488126	-0.591490	0.346836
25	1	0	4.826493	0.183540	-0.341784
26	1	0	4.519429	-0.179998	1.356484
27	1	0	5.151121	-1.450323	0.286407

7, R=COMe^b (G=-687.994759 Hartrees)

1	6	0	-0.093305	-1.844247	0.067677
2	6	0	-1.543574	-2.209697	0.345206
3	6	0	-1.729411	-0.721787	0.809141
4	6	0	-0.258525	-0.517658	0.467549
5	1	0	-1.704809	-2.946890	1.133260
6	1	0	-2.146671	-2.466273	-0.525665
7	1	0	-1.966598	-0.595900	1.868883
8	6	0	-2.676161	0.112190	-0.013041
9	8	0	-3.457682	-0.300001	-0.857854
10	6	0	0.761648	0.423072	0.448862
11	6	0	1.138845	-2.329760	-0.363543
12	1	0	1.298665	-3.355581	-0.674892
13	6	0	2.013819	-0.054079	0.005359
14	6	0	2.185728	-1.399149	-0.393987

15	8	0	-2.530804	1.423721	0.306439
16	6	0	-3.383122	2.321235	-0.441989
17	1	0	-4.427807	2.067814	-0.278730
18	1	0	-3.153325	2.255847	-1.502851
19	1	0	-3.157410	3.308863	-0.055398
20	1	0	0.610133	1.449354	0.758685
21	6	0	3.206517	0.849792	-0.074428
22	1	0	3.174135	-1.694805	-0.723534
23	8	0	4.313378	0.409063	-0.400723
24	6	0	3.029516	2.317208	0.248404
25	1	0	2.282435	2.769094	-0.405197
26	1	0	2.695244	2.446862	1.278684
27	1	0	3.985021	2.816641	0.112610

7, R=CHO^a (G=-648.828169 Hartrees)

1	6	0	0.399640	-1.727159	0.047919
2	6	0	-1.002232	-2.225956	0.361726
3	6	0	-1.319873	-0.760140	0.822175
4	6	0	0.118372	-0.416846	0.452092
5	1	0	-1.072168	-2.969251	1.157286
6	1	0	-1.597130	-2.545573	-0.493751
7	1	0	-1.548869	-0.646748	1.884668
8	6	0	-2.351352	-0.024023	0.006891
9	8	0	-3.069007	-0.507942	-0.856846
10	6	0	1.041413	0.614613	0.408705
11	6	0	1.657139	-2.103489	-0.411414
12	1	0	1.901364	-3.112262	-0.723008
13	6	0	2.316440	0.243759	-0.066640
14	6	0	2.611741	-1.075541	-0.469432
15	8	0	-2.359462	1.286093	0.353560
16	6	0	-3.287503	2.103036	-0.397543
17	1	0	-4.302439	1.738488	-0.259040
18	1	0	-3.031634	2.080854	-1.454119
19	1	0	-3.172631	3.101402	0.009286
20	1	0	0.842233	1.635456	0.711913
21	6	0	3.386901	1.260844	-0.171037
22	1	0	3.613442	-1.293242	-0.826850
23	8	0	3.252006	2.445126	0.134082
24	1	0	4.355419	0.890049	-0.553401

7, R=CHO^b (G=-648.827854 Hartrees)

1	6	0	-0.380521	1.618443	0.027624
2	6	0	1.007490	2.192974	0.265891
3	6	0	1.404274	0.766716	0.787136
4	6	0	-0.027377	0.345987	0.481377
5	1	0	1.071847	2.978572	1.020232
6	1	0	1.559363	2.493476	-0.624645
7	1	0	1.669679	0.720434	1.846572
8	6	0	2.448888	0.038620	-0.017881
9	8	0	3.159187	0.523038	-0.886918
10	6	0	-0.914413	-0.720861	0.518111
11	6	0	-1.671369	1.917360	-0.405945

12	1	0	-1.966942	2.899601	-0.755822
13	6	0	-2.218689	-0.428864	0.072405
14	6	0	-2.585807	0.856723	-0.382323
15	8	0	2.486576	-1.266619	0.350605
16	6	0	3.446925	-2.068368	-0.375896
17	1	0	4.448628	-1.669607	-0.235440
18	1	0	3.201472	-2.074764	-1.435182
19	1	0	3.360205	-3.061983	0.049368
20	1	0	-0.645397	-1.713570	0.864475
21	6	0	-3.223200	-1.517169	0.069837
22	1	0	-3.608729	0.999150	-0.710385
23	8	0	-4.389696	-1.392257	-0.300579
24	1	0	-2.855867	-2.493984	0.433953

7, R=NO₂ (G=-739.816446 Hartrees)

1	6	0	0.001859	1.801907	0.028983
2	6	0	1.436311	2.233055	0.293254
3	6	0	1.682223	0.768094	0.799798
4	6	0	0.222980	0.493124	0.464677
5	1	0	1.568088	2.999750	1.057862
6	1	0	2.026371	2.486318	-0.587269
7	1	0	1.920883	0.681316	1.862824
8	6	0	2.661939	-0.052599	0.000106
9	8	0	3.428812	0.370618	-0.852470
10	6	0	-0.749004	-0.497161	0.466786
11	6	0	-1.245060	2.223938	-0.421662
12	1	0	-1.446216	3.231573	-0.765011
13	6	0	-1.995042	-0.051234	0.006407
14	6	0	-2.260919	1.255700	-0.428702
15	8	0	2.560756	-1.356628	0.353349
16	6	0	3.439502	-2.248750	-0.372620
17	1	0	4.476009	-1.962112	-0.212962
18	1	0	3.208912	-2.214185	-1.434566
19	1	0	3.238860	-3.232144	0.037203
20	1	0	-0.594345	-1.518569	0.785839
21	7	0	-3.100855	-1.022577	-0.034052
22	8	0	-2.802514	-2.230940	0.004478
23	8	0	-4.262109	-0.578929	-0.101082
24	1	0	-3.260878	1.496680	-0.761923

TS for 7→9, R=CN (G=-627.753222 Hartrees)

1	6	0	-0.206437	1.246650	0.311338
2	6	0	0.951036	1.794238	0.929834
3	6	0	1.081642	-0.537310	0.932701
4	6	0	-0.263190	-0.128454	0.667201
5	1	0	1.099676	1.598263	1.982589
6	1	0	1.509084	2.625723	0.504571
7	1	0	1.329790	-1.266525	1.702101
8	6	0	2.106826	-0.390288	-0.131745
9	8	0	1.919760	-0.077308	-1.301387
10	6	0	-1.472172	-0.834526	0.629165
11	6	0	-1.227746	1.824186	-0.469604

12	1	0	-1.151434	2.831926	-0.860861
13	6	0	-2.534026	-0.203561	-0.031314
14	6	0	-2.400957	1.094305	-0.603239
15	8	0	3.323984	-0.753628	0.364827
16	6	0	4.393517	-0.715444	-0.604790
17	1	0	4.523396	0.296802	-0.981575
18	1	0	4.175155	-1.385367	-1.433081
19	1	0	5.273865	-1.042031	-0.061937
20	1	0	-1.566199	-1.856197	0.979665
21	6	0	-3.785806	-0.892658	-0.170732
22	7	0	-4.821989	-1.458587	-0.279200
23	1	0	-3.245494	1.512175	-1.137486

TS for 7→8, R=CN (G=-627.756262 Hartrees)

1	6	0	0.661746	1.771967	0.182642
2	6	0	-0.407078	2.639507	0.555284
3	6	0	-1.268550	0.837287	-0.580705
4	6	0	0.075760	0.527902	-0.173151
5	1	0	-0.374363	3.717808	0.413719
6	1	0	-1.115028	2.275044	1.287078
7	1	0	-1.396747	1.581461	-1.355874
8	6	0	-2.448015	-0.016892	-0.354240
9	8	0	-3.570089	0.212113	-0.795999
10	6	0	0.829371	-0.652541	-0.166710
11	6	0	2.060845	1.937821	0.156708
12	1	0	2.528264	2.903543	0.311112
13	6	0	2.217927	-0.497624	-0.056248
14	6	0	2.827400	0.782129	0.068014
15	8	0	-2.146316	-1.083901	0.434191
16	6	0	-3.261014	-1.969830	0.686668
17	1	0	-3.640997	-2.369344	-0.250689
18	1	0	-4.053854	-1.432202	1.201296
19	1	0	-2.855465	-2.758048	1.311244
20	1	0	0.387424	-1.626966	-0.331592
21	6	0	3.059132	-1.660157	-0.110573
22	7	0	3.751228	-2.622073	-0.149710
23	1	0	3.908265	0.840102	0.109999

TS for 7→9, R=NO^a (G=-664.726156 Hartrees)

1	6	0	-0.166855	1.288843	0.368983
2	6	0	0.982048	1.765933	1.054377
3	6	0	1.063767	-0.571396	0.892032
4	6	0	-0.265982	-0.109976	0.629443
5	1	0	1.105709	1.480657	2.090012
6	1	0	1.564310	2.617238	0.708632
7	1	0	1.277347	-1.355365	1.616605
8	6	0	2.113627	-0.378686	-0.139701
9	8	0	1.957202	0.018581	-1.288138
10	6	0	-1.483346	-0.785007	0.511362
11	6	0	-1.147203	1.944510	-0.404264
12	1	0	-1.032484	2.973772	-0.723172
13	6	0	-2.499953	-0.074674	-0.136504

14	6	0	-2.329507	1.248585	-0.617494
15	8	0	3.311738	-0.805224	0.352934
16	6	0	4.401069	-0.726839	-0.591865
17	1	0	4.562590	0.305550	-0.894537
18	1	0	4.183343	-1.331870	-1.468846
19	1	0	5.262311	-1.112473	-0.057167
20	1	0	-1.624140	-1.825734	0.779563
21	7	0	-3.799837	-0.631281	-0.411815
22	8	0	-3.961922	-1.793709	0.007116
23	1	0	-3.162251	1.702254	-1.141900

TS for 7→8, R=NO^a (G=-664.729434 Hartrees)

1	6	0	0.729222	1.746589	0.084366
2	6	0	-0.363439	2.585634	0.450306
3	6	0	-1.188072	0.620104	-0.421279
4	6	0	0.199934	0.436064	-0.091859
5	1	0	-0.408529	3.644376	0.203670
6	1	0	-0.992880	2.257226	1.266378
7	1	0	-1.425772	1.259274	-1.261846
8	6	0	-2.226909	-0.323717	0.023698
9	8	0	-2.029428	-1.275735	0.775115
10	6	0	1.016399	-0.695537	-0.024036
11	6	0	2.108110	1.991141	-0.076834
12	1	0	2.520142	2.993482	-0.060660
13	6	0	2.392245	-0.436944	-0.047527
14	6	0	2.931728	0.871755	-0.105983
15	8	0	-3.440449	-0.004559	-0.494445
16	6	0	-4.512373	-0.883637	-0.083997
17	1	0	-4.609228	-0.874928	0.999250
18	1	0	-4.314499	-1.897582	-0.423487
19	1	0	-5.400368	-0.480862	-0.558219
20	1	0	0.637930	-1.709295	-0.052452
21	7	0	3.392351	-1.475073	-0.055758
22	8	0	2.934349	-2.632663	-0.006505
23	1	0	4.009904	0.968766	-0.156775

TS for 7→9, R=NO^b (G=-664.726777 Hartrees)

1	6	0	-0.184357	1.193231	0.338750
2	6	0	0.965560	1.799512	0.915910
3	6	0	1.203953	-0.511230	0.957356
4	6	0	-0.167615	-0.175205	0.721926
5	1	0	1.148120	1.632343	1.968491
6	1	0	1.478686	2.644206	0.460953
7	1	0	1.510302	-1.206392	1.737386
8	6	0	2.188980	-0.347306	-0.142521
9	8	0	1.953204	-0.065961	-1.311212
10	6	0	-1.344984	-0.933214	0.717225
11	6	0	-1.251066	1.714269	-0.428621
12	1	0	-1.222212	2.718684	-0.835149
13	6	0	-2.438535	-0.356525	0.066485
14	6	0	-2.392298	0.934234	-0.526609
15	8	0	3.434596	-0.650026	0.322734

16	6	0	4.472014	-0.586788	-0.679992
17	1	0	4.547412	0.422200	-1.079666
18	1	0	4.257343	-1.281849	-1.488274
19	1	0	5.381271	-0.865339	-0.158472
20	1	0	-1.411475	-1.953057	1.080716
21	7	0	-3.601480	-1.199419	0.029249
22	8	0	-4.577163	-0.708186	-0.572537
23	1	0	-3.274089	1.292647	-1.042073

TS for 7→8, R=NO^b (G=-664.730070 Hartrees)

1	6	0	0.641508	1.640648	0.082283
2	6	0	-0.449221	2.493499	0.428143
3	6	0	-1.287479	0.550831	-0.430410
4	6	0	0.095665	0.342813	-0.095676
5	1	0	-0.484994	3.549104	0.165924
6	1	0	-1.081492	2.185583	1.250008
7	1	0	-1.511851	1.182919	-1.279891
8	6	0	-2.342966	-0.374197	0.017843
9	8	0	-2.158370	-1.331433	0.765704
10	6	0	0.907280	-0.795664	-0.015765
11	6	0	2.029675	1.865261	-0.057526
12	1	0	2.451089	2.863971	-0.037127
13	6	0	2.284968	-0.558992	-0.028719
14	6	0	2.846680	0.744251	-0.076953
15	8	0	-3.552779	-0.031028	-0.492208
16	6	0	-4.639180	-0.890186	-0.077116
17	1	0	-4.728515	-0.882805	1.006761
18	1	0	-4.463465	-1.906703	-0.421000
19	1	0	-5.522161	-0.468545	-0.544204
20	1	0	0.526205	-1.809457	-0.037851
21	7	0	3.081035	-1.756103	-0.016900
22	8	0	4.311377	-1.558571	-0.066741
23	1	0	3.924529	0.837318	-0.114987

TS for 7→9, R=COMe^a (G=-687.934058 Hartrees)

1	6	0	-0.265324	1.300569	-0.468598
2	6	0	-1.465427	1.741617	-1.091886
3	6	0	-1.489210	-0.586242	-0.882941
4	6	0	-0.155428	-0.097579	-0.703065
5	1	0	-1.638547	1.445422	-2.117208
6	1	0	-2.046476	2.584594	-0.723434
7	1	0	-1.728032	-1.391516	-1.575724
8	6	0	-2.485565	-0.388229	0.198030
9	8	0	-2.278244	0.030441	1.331147
10	6	0	1.081317	-0.747039	-0.634761
11	6	0	0.753335	1.981426	0.225218
12	1	0	0.649987	3.018416	0.523737
13	6	0	2.139786	-0.032833	-0.060097
14	6	0	1.956006	1.303878	0.392328
15	8	0	-3.703581	-0.839921	-0.223295
16	6	0	-4.740965	-0.760296	0.776755
17	1	0	-4.901516	0.274626	1.071633

18	1	0	-4.468754	-1.347350	1.650879
19	1	0	-5.624416	-1.166373	0.295813
20	1	0	1.219894	-1.789117	-0.899511
21	6	0	3.454276	-0.735241	0.088474
22	1	0	2.779658	1.820665	0.868209
23	8	0	3.623633	-1.854461	-0.407081
24	6	0	4.566995	-0.057376	0.855803
25	1	0	4.858483	0.873770	0.367748
26	1	0	4.246346	0.182005	1.870398
27	1	0	5.420134	-0.729541	0.889737

TS for 7→8, R=COMe^a (G=-687.936622 Hartrees)

1	6	0	0.174525	1.903072	0.063782
2	6	0	-0.996141	2.637382	0.419750
3	6	0	-1.623186	0.591327	-0.422417
4	6	0	-0.221731	0.549091	-0.099274
5	1	0	-1.144249	3.683218	0.157506
6	1	0	-1.586726	2.264589	1.245603
7	1	0	-1.926455	1.190372	-1.271320
8	6	0	-2.564564	-0.440233	0.042442
9	8	0	-2.285389	-1.339848	0.831440
10	6	0	0.707208	-0.493437	-0.026229
11	6	0	1.524830	2.268339	-0.093540
12	1	0	1.845466	3.304096	-0.085537
13	6	0	2.061648	-0.133498	-0.051106
14	6	0	2.453563	1.231470	-0.114492
15	8	0	-3.798141	-0.266635	-0.501770
16	6	0	-4.778713	-1.236313	-0.070430
17	1	0	-4.892183	-1.199191	1.010720
18	1	0	-4.472792	-2.236237	-0.369205
19	1	0	-5.696974	-0.945668	-0.568714
20	1	0	0.423881	-1.538249	-0.043705
21	6	0	3.076592	-1.235262	-0.045216
22	1	0	3.505704	1.480542	-0.171190
23	8	0	2.723144	-2.414374	-0.149409
24	6	0	4.540291	-0.882531	0.103735
25	1	0	4.883420	-0.299667	-0.752396
26	1	0	4.706744	-0.288066	1.002769
27	1	0	5.111316	-1.805320	0.161370

TS for 7→9, R=COMe^b (G=-687.934614 Hartrees)

1	6	0	0.270653	1.329102	0.449889
2	6	0	1.472916	1.731995	1.096349
3	6	0	1.443497	-0.584924	0.875138
4	6	0	0.125059	-0.066032	0.670024
5	1	0	1.617292	1.431150	2.124761
6	1	0	2.082839	2.560829	0.742450
7	1	0	1.650663	-1.397432	1.570158
8	6	0	2.467531	-0.408299	-0.183743
9	8	0	2.294410	0.015709	-1.320234
10	6	0	-1.127851	-0.686732	0.571523
11	6	0	-0.722331	2.043430	-0.251663

12	1	0	-0.587319	3.079942	-0.538926
13	6	0	-2.159639	0.061235	-0.009095
14	6	0	-1.937560	1.400606	-0.437636
15	8	0	3.665834	-0.887109	0.264113
16	6	0	4.727837	-0.824576	-0.711295
17	1	0	4.915630	0.208014	-0.997974
18	1	0	4.464610	-1.402744	-1.594042
19	1	0	5.591564	-1.249895	-0.211542
20	1	0	-1.256122	-1.732776	0.824768
21	6	0	-3.521563	-0.519395	-0.220672
22	1	0	-2.766074	1.914980	-0.908143
23	8	0	-4.415751	0.152376	-0.747157
24	6	0	-3.788627	-1.941033	0.222573
25	1	0	-3.156128	-2.639443	-0.327349
26	1	0	-3.579519	-2.062947	1.285898
27	1	0	-4.832916	-2.169743	0.027814

TS for 7→8, R=COMe^b (G=-687.938384 Hartrees)

1	6	0	0.181639	1.938760	0.099291
2	6	0	-1.009661	2.639571	0.460689
3	6	0	-1.592943	0.617832	-0.425004
4	6	0	-0.192283	0.585619	-0.098670
5	1	0	-1.181315	3.685649	0.213256
6	1	0	-1.588439	2.246294	1.285486
7	1	0	-1.905406	1.231294	-1.259995
8	6	0	-2.514041	-0.448592	0.001507
9	8	0	-2.199605	-1.403850	0.708911
10	6	0	0.753402	-0.446353	-0.036616
11	6	0	1.529033	2.329712	-0.037625
12	1	0	1.832223	3.369989	0.001316
13	6	0	2.101106	-0.062676	-0.043265
14	6	0	2.471728	1.309936	-0.073929
15	8	0	-3.767908	-0.244826	-0.478800
16	6	0	-4.728618	-1.248606	-0.081559
17	1	0	-4.797163	-1.293195	1.003002
18	1	0	-4.434311	-2.221826	-0.467483
19	1	0	-5.666997	-0.925175	-0.518226
20	1	0	0.448366	-1.483783	-0.076002
21	6	0	3.198589	-1.078981	-0.043870
22	1	0	3.529382	1.539492	-0.111277
23	8	0	4.378973	-0.729208	-0.158029
24	6	0	2.838542	-2.540395	0.103438
25	1	0	2.242515	-2.706390	1.001257
26	1	0	2.252461	-2.877372	-0.753003
27	1	0	3.758056	-3.116878	0.158681

TS for 7→9, R=CHO^a (G=-648.767703 Hartrees)

1	6	0	-0.130938	1.298133	0.369994
2	6	0	1.029201	1.760365	1.049450
3	6	0	1.078935	-0.574361	0.888520
4	6	0	-0.245476	-0.097608	0.629305
5	1	0	1.150028	1.480976	2.086938

6	1	0	1.622740	2.601787	0.698120
7	1	0	1.285066	-1.363585	1.609581
8	6	0	2.129606	-0.391165	-0.143329
9	8	0	1.978467	0.006747	-1.292505
10	6	0	-1.475177	-0.753763	0.515551
11	6	0	-1.110649	1.964397	-0.392904
12	1	0	-0.989193	2.993663	-0.710171
13	6	0	-2.497396	-0.045222	-0.126035
14	6	0	-2.300684	1.278196	-0.602880
15	8	0	3.324897	-0.829543	0.348621
16	6	0	4.413143	-0.762864	-0.597434
17	1	0	4.584939	0.267497	-0.901621
18	1	0	4.188629	-1.366402	-1.473816
19	1	0	5.271521	-1.156535	-0.063804
20	1	0	-1.627454	-1.791341	0.792585
21	6	0	-3.807523	-0.694310	-0.355800
22	1	0	-3.115060	1.764900	-1.130071
23	8	0	-4.093157	-1.832089	0.016805
24	1	0	-4.551116	-0.082672	-0.897734

TS for 7→8, R=CHO^a (G=-648.770584 Hartrees)

1	6	0	0.681752	1.776425	0.079595
2	6	0	-0.426728	2.598486	0.440194
3	6	0	-1.213663	0.614257	-0.421648
4	6	0	0.177516	0.457477	-0.092491
5	1	0	-0.490157	3.655019	0.187402
6	1	0	-1.048998	2.265093	1.259625
7	1	0	-1.463939	1.245084	-1.264809
8	6	0	-2.235987	-0.344522	0.028512
9	8	0	-2.027823	-1.279349	0.798245
10	6	0	1.019577	-0.656481	-0.018139
11	6	0	2.056501	2.041606	-0.075544
12	1	0	2.453149	3.050434	-0.060102
13	6	0	2.394723	-0.390703	-0.040836
14	6	0	2.898538	0.934419	-0.100768
15	8	0	-3.451995	-0.059555	-0.506332
16	6	0	-4.508303	-0.953517	-0.089253
17	1	0	-4.615583	-0.927344	0.992797
18	1	0	-4.286052	-1.969237	-0.407866
19	1	0	-5.400529	-0.578887	-0.578555
20	1	0	0.657651	-1.677233	-0.037979
21	6	0	3.362064	-1.511475	-0.045740
22	1	0	3.973047	1.079181	-0.153211
23	8	0	3.049644	-2.701370	-0.023128
24	1	0	4.426860	-1.215756	-0.070875

TS for 7→9, R=CHO^b (G=-648.768213 Hartrees)

1	6	0	0.151948	1.203569	-0.343201
2	6	0	-1.006963	1.791613	-0.922894
3	6	0	-1.214913	-0.525492	-0.945605
4	6	0	0.151331	-0.168321	-0.713489

5	1	0	-1.188612	1.616161	-1.974199
6	1	0	-1.527608	2.634796	-0.473416
7	1	0	-1.511358	-1.234074	-1.717551
8	6	0	-2.204595	-0.359950	0.148397
9	8	0	-1.976340	-0.072504	1.317277
10	6	0	1.339423	-0.911507	-0.704363
11	6	0	1.214732	1.741538	0.414427
12	1	0	1.179260	2.749205	0.812318
13	6	0	2.437644	-0.327470	-0.065448
14	6	0	2.362869	0.969644	0.512960
15	8	0	-3.448262	-0.672009	-0.319685
16	6	0	-4.488599	-0.606833	0.679152
17	1	0	-4.569981	0.404320	1.072278
18	1	0	-4.273919	-1.295432	1.493048
19	1	0	-5.395319	-0.892656	0.156951
20	1	0	1.387716	-1.934141	-1.068047
21	6	0	3.693927	-1.100276	0.029281
22	1	0	3.242082	1.344187	1.023268
23	8	0	4.720983	-0.696770	0.574772
24	1	0	3.665868	-2.101201	-0.438867

TS for 7→8, R=CHO^b (G=-648.771944 Hartrees)

1	6	0	0.603554	1.672515	0.081226
2	6	0	-0.501298	2.506847	0.431621
3	6	0	-1.308573	0.552494	-0.430244
4	6	0	0.078534	0.366854	-0.099889
5	1	0	-0.554676	3.562340	0.171230
6	1	0	-1.123066	2.189526	1.257848
7	1	0	-1.548022	1.186960	-1.273691
8	6	0	-2.345330	-0.396405	0.009755
9	8	0	-2.139668	-1.371310	0.729647
10	6	0	0.908790	-0.759043	-0.021258
11	6	0	1.986717	1.915688	-0.057931
12	1	0	2.396765	2.919068	-0.034453
13	6	0	2.286823	-0.516257	-0.030693
14	6	0	2.815499	0.801622	-0.079353
15	8	0	-3.567549	-0.056686	-0.473660
16	6	0	-4.636584	-0.939047	-0.063833
17	1	0	-4.710408	-0.958810	1.021087
18	1	0	-4.453807	-1.944972	-0.434343
19	1	0	-5.531692	-0.517860	-0.507804
20	1	0	0.514250	-1.769206	-0.042994
21	6	0	3.207729	-1.672617	-0.016778
22	1	0	3.892661	0.911842	-0.117990
23	8	0	4.435297	-1.586141	-0.057407
24	1	0	2.718194	-2.661691	0.036736

TS for 7→9, R=NO₂ (G=-739.756559 Hartrees)

1	6	0	-0.207504	1.293758	-0.463711
2	6	0	-1.393333	1.732803	-1.113775
3	6	0	-1.432306	-0.592450	-0.879710
4	6	0	-0.100884	-0.107078	-0.681272

5	1	0	-1.550451	1.424453	-2.137990
6	1	0	-1.980874	2.577963	-0.761910
7	1	0	-1.659802	-1.406348	-1.565938
8	6	0	-2.446653	-0.379465	0.183899
9	8	0	-2.257007	0.066400	1.309345
10	6	0	1.132568	-0.765301	-0.590709
11	6	0	0.801454	1.983479	0.238394
12	1	0	0.693912	3.023120	0.524191
13	6	0	2.152518	-0.017624	-0.012913
14	6	0	2.003480	1.315419	0.433621
15	8	0	-3.651994	-0.849492	-0.246341
16	6	0	-4.707563	-0.757447	0.735068
17	1	0	-4.880254	0.282180	1.004876
18	1	0	-4.444563	-1.324251	1.625036
19	1	0	-5.579127	-1.180633	0.247637
20	1	0	1.276982	-1.809537	-0.835553
21	7	0	3.458235	-0.665035	0.181882
22	8	0	3.670084	-1.729052	-0.429299
23	8	0	4.271576	-0.109071	0.944482
24	1	0	2.844594	1.801445	0.907629

TS for 7→8, R=NO₂ (G=-739.759845 Hartrees)

1	6	0	0.253490	1.883254	0.114769
2	6	0	-0.909070	2.628302	0.474805
3	6	0	-1.561933	0.617162	-0.418963
4	6	0	-0.166522	0.541143	-0.082179
5	1	0	-1.043021	3.678846	0.225262
6	1	0	-1.512201	2.249610	1.288678
7	1	0	-1.845422	1.248745	-1.250974
8	6	0	-2.519377	-0.420535	-0.001316
9	8	0	-2.240576	-1.375758	0.719961
10	6	0	0.738822	-0.525985	-0.016809
11	6	0	1.611909	2.231732	-0.019212
12	1	0	1.948777	3.261060	0.019814
13	6	0	2.078446	-0.150322	-0.021727
14	6	0	2.529391	1.187506	-0.058518
15	8	0	-3.756385	-0.186479	-0.507497
16	6	0	-4.751146	-1.163072	-0.123290
17	1	0	-4.843018	-1.196831	0.959856
18	1	0	-4.472545	-2.145913	-0.495865
19	1	0	-5.671249	-0.819236	-0.582402
20	1	0	0.442138	-1.564903	-0.051839
21	7	0	3.094692	-1.213055	-0.031369
22	8	0	2.732646	-2.358938	0.293135
23	8	0	4.253911	-0.900391	-0.365723
24	1	0	3.592875	1.377429	-0.097311

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