

# The relative electron acceptor abilities of the NO<sub>2</sub>, NO and CHO groups and their application to the NBO-TS torquoselectivity

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**Abstract.** Much against the long held notion in the prediction of torquoselectivity, the relative  $\pi$ - and  $\sigma$ -acceptor abilities of NO<sub>2</sub>, NO and CHO are demonstrated to decrease in the order NO<sub>2</sub> > NO > CHO from a combination of different computational parameters such as the differential electron densities, antiperiplanar  $\sigma_{\text{CH/CC}}-\sigma^*_{\text{CN}}$  and  $\sigma_{\text{CH/CC}}-\sigma^*_{\text{CO}}$  interactions, and conjugate interactions such as  $\sigma_{\text{CH/CC}}-\pi^*_{\text{NO}}$  and  $\pi_{\text{CC}}-\pi^*_{\text{NO}}$  in the nitro and nitroso species and  $\sigma_{\text{CH/CC}}-\pi^*_{\text{CO}}$  and  $\pi_{\text{CC}}-\pi^*_{\text{CO}}$  in the CHO species.

**Keywords:**  $\pi$ -acceptor ability,  $\sigma$ -acceptor ability, thermal ring opening of 3-substituted cyclobutene, torquoselectivity,  $\sigma \rightarrow \pi^*$  interaction

## Introduction

3-Substituted cyclobutenes open, under thermal conditions, in a conrotatory fashion to generate 1,3-dienes.<sup>1</sup> The substituent ends up on a *trans* or a *cis* double bond in the product diene depending on its electronic nature in a process termed torquoselectivity. Overall, (a) an electron releasing substituent (ERS) is demonstrated to rotate outward to allow it reside on a *trans* double bond as in the transformation **1**→**2** and (b) an electron withdrawing substituent rotates inward to allow it reside on a *cis* double bond as in the transformation **3**→**4** as shown in [Figure 1](#). During the investigation of torquoselectivity of ring opening from the differential transition state energies, Houk predicted inward rotation of the formyl (CHO) and nitroso (NO) groups and outward rotation of the nitro (NO<sub>2</sub>) group.<sup>2</sup> Houk asserted that NO<sub>2</sub> was a relatively poor resonance acceptor from a comparison of the Taft  $\sigma_{\text{R}}^{\circ}$  values. That NO<sub>2</sub> was a poorer resonance acceptor than NO and CHO caught our attention for our own recent interest in torquoselectivity.<sup>3</sup> We felt the contrary and, thus, chose to investigate. The relative resonance accepting ability of NO<sub>2</sub>, NO and CHO has not been systematically investigated till date.<sup>4</sup> It is important to note that while 3-CHO-cyclobutene opens exclusively inward, the experimental selectivities of 3-NO- and 3-NO<sub>2</sub>-cyclobutenes are not reported.<sup>5</sup>

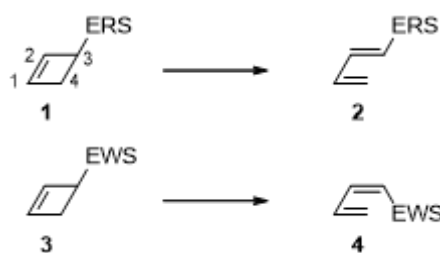


Figure 1. The outward and inward openings of 3-substituted cyclobutenes **1** and **3**

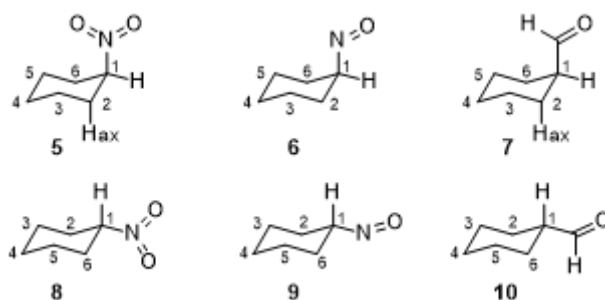
**Computational methods.** All the geometry optimizations were carried at the MP2/cc-pVTZ//MP2/6-31G(d) level at 298.15 K using Gaussian 09 set of programs.<sup>6</sup>

**Results and Discussion.** In the context of torquoselectivity of 3-substituted cyclobutenes, the substituents influence the ring opening by either or a combination of  $\sigma_{C3C4} \rightarrow \pi^*_{NO/CO}$  and  $\sigma_{C3C4} \rightarrow \sigma^*_{NO/CO}$  interactions. The  $\sigma_{C3C4} \rightarrow \pi^*_{NO/CO}$  interaction originates from the  $\sigma_{C3C4}$  orbital being parallel to the  $\pi$  orbital of the substituent. Likewise,  $\sigma_{C3C4} \rightarrow \sigma^*_{NO/CO}$  interaction arises from  $\sigma_{C3C4}$  orbital being antiperiplanar to the  $\sigma$  orbital of the substituent. While  $\sigma_{C3C4} \rightarrow \pi^*_{NO/CO}$  interaction is typical of allyl anion like resonance interaction,  $\sigma_{C3C4} \rightarrow \sigma^*_{NO/CO}$  interaction is akin to antiperiplanar interaction.<sup>7</sup> The intensity of interaction will depend on the resonance accepting ability of the substituent in  $\sigma_{C3C4} \rightarrow \pi^*_{NO/CO}$  interaction and  $\sigma$ -electron accepting ability in  $\sigma_{C3C4} \rightarrow \sigma^*_{NO/CO}$  interaction; the greater the ability, the more the interaction.

In the instance where the group is located on a carbon-carbon  $\pi$ -bond as in  $CH_2=CHX$  ( $X = NO_2$ ,  $NO$  and  $CHO$ ),  $\pi_{CC} \rightarrow \pi^*_{NO/CO}$  interaction will constitute a meaningful estimate of the resonance acceptor ability. The larger the interaction, the larger will be the resonance acceptor ability of the group. Further, the larger the  $\pi_{CC} \rightarrow \pi^*_{NO/CO}$  interaction, the lower will be the LUMO of the conjugated system.<sup>8</sup> Thus, an estimate of the LUMO energy can provide an estimate of the resonance acceptor ability, in inverse relationship.

The antiperiplanar interaction of a  $\sigma$  bond with  $\sigma^*_{CN}$  in the  $NO_2$  and  $NO$  species and  $\sigma^*_{CC(=O)}$  in the  $CHO$  species in a geometrically well-defined arrangement, such as in substituted cyclohexane, provides a reasonably good measure of the  $\sigma$ -electron attracting ability of the substituent. For instance, the  $\sigma_{C2H_{ax}} \rightarrow \sigma^*_{C1X}$  ( $X = N$ ,  $C(=O)$ ) interaction in **5–7** and

$\sigma_{C2C3} \rightarrow \sigma_{C1X}^*$  interaction in **8-10**, [Figure 2](#), are destined to indicate the relative  $\sigma$ -electron attracting strengths.  $\text{MeCH}_2\text{NO}_2$ ,  $\text{MeCH}_2\text{NO}$  and  $\text{MeCH}_2\text{CHO}$  could also serve as excellent similar tools, must the conformation in the lowest ground state structure be the same.



**Figure 2.** The lowest energy conformers of cyclohexanes bearing axial and equatorial  $\text{NO}_2$ ,  $\text{NO}$  and  $\text{CHO}$  substituents

The Mulliken atomic charges and also the Natural Charges on the nitrogen atoms in species **5-6** and also **8-9** may provide a measure of electron deficiency on these centres to correlate with the relative electron accepting abilities of  $\text{NO}_2$  and  $\text{NO}$  groups.

The details of the results are as follows:

1. The LUMO energies of  $\text{CH}_2=\text{CHNO}_2$ ,  $\text{CH}_2=\text{CHNO}$  and  $\text{CH}_2=\text{CHCHO}$  were estimated at 28.0, 33.8 and 49.7 kcal/mol, respectively, indicating larger resonance acceptor ability of  $\text{NO}_2$  over both  $\text{NO}$  and  $\text{CHO}$  groups. The overall decreasing order of resonance acceptor ability, therefore, is  $\text{NO}_2 > \text{NO} > \text{CHO}$ .
2. The  $\sigma_{C2\text{Hax}} \rightarrow \sigma_{\text{CN}}$  interaction measures 6.8 and 4.9 kcal/mol in the lowest energy conformers of **5** and **6**, respectively. These numbers favor greater  $\sigma$ -electron attracting ability of  $\text{NO}_2$  than  $\text{NO}$ . The corresponding interaction  $\sigma_{C2\text{Hax}} \rightarrow \sigma_{\text{CC}(=\text{O})}$  in **7** is 4.5 kcal/mol. The decreasing order of antiperiplanar  $\sigma$ -electron acceptor ability, therefore, is  $\text{NO}_2 > \text{NO} > \text{CHO}$ .
3. The  $\sigma_{C2C3} \rightarrow \sigma_{\text{CN}}$  interaction measures 4.5 and 3.0 kcal/mol in the conformers **8** and **9**, respectively. These numbers favor  $\text{NO}_2$  over  $\text{NO}$  as the better  $\sigma$ -electron acceptor. The corresponding  $\sigma_{C2C3} \rightarrow \sigma_{\text{CC}(=\text{O})}$  interaction in **10** is 2.7 kcal/mol. Thus, again, the relative order of  $\sigma$ -electron acceptor ability is  $\text{NO}_2 > \text{NO} > \text{CHO}$ .

4. The Mulliken atomic charges on the N atoms in **5** and **6** are 0.47 and 0.07, respectively. Likewise, the Natural charges on these N atoms are 0.63 and 0.17, respectively. The much larger positive charge on N in **5** supports greater electron deficiency and, thus, a greater electron attracting ability of NO<sub>2</sub> over NO.
5. The Mulliken atomic charges on the N atoms in **8** and **9** are 0.46 and 0.07, respectively. The corresponding Natural charges are, respectively, 0.64 and 0.18. The significantly larger positive charge on the N in **8** supports, once again, greater electron deficiency and, thus, a greater electron accepting ability of NO<sub>2</sub> over NO.
6. In the lowest energy conformer around  $\sigma_{\text{CN}}$  in MeCH<sub>2</sub>NO<sub>2</sub>,  $\sigma_{\text{CMe}}$  is orthogonal to the NO<sub>2</sub> plane, as shown in **11** in Figure 3. However, the same is synperiplanar with the NO group in MeCH<sub>2</sub>NO, as shown in **12**. This conformational difference does not permit comparison of the two species. However, the conformation of MeCH<sub>2</sub>CHO, **13**, is very similar to that of MeCH<sub>2</sub>NO. This allows a reliable comparison of their electronic properties. Being orthogonal,  $\sigma_{\text{C1C2}}$  does not interact with  $\pi^*_{\text{NO}}$  in **12** and  $\pi^*_{\text{CO}}$  in **13**. The antiperiplanar interactions  $\sigma_{\text{C2H}} \rightarrow \sigma^*_{\text{CN}}$  in **12** and  $\sigma_{\text{C2H}} \rightarrow \sigma^*_{\text{CC(=O)}}$  in **13** measure, respectively, 6.2 and 4.6 kcal/mol. The interactions  $\sigma_{\text{C1H}} \rightarrow \pi^*_{\text{NO}}$  in **12** and  $\sigma_{\text{C2H}} \rightarrow \sigma^*_{\text{C1C(=O)}}$  in **13** measure, respectively, 14.6 and 15.1 kcal/mol. Since the total sum of the above  $\sigma \rightarrow \sigma^*$  and  $\sigma \rightarrow \pi^*$  interactions is larger in MeCH<sub>2</sub>NO by 2.1 kcal/mol, the NO group is an overall better acceptor than CHO group.

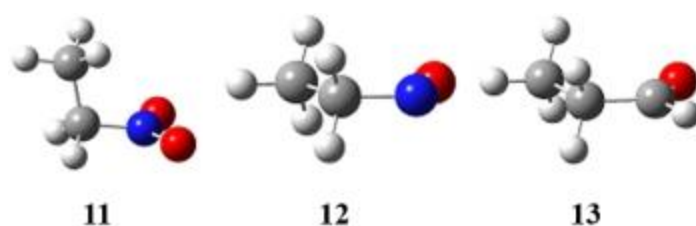


Figure 3. The lowest energy conformers of MeCH<sub>2</sub>NO<sub>2</sub> (**11**), MeCH<sub>2</sub>NO (**12**) and MeCH<sub>2</sub>CHO (**13**)

## Conclusion

From a combination of various approaches such as the LUMO energy when the functional group is in conjugation with a  $\pi$ -bond, antiperiplanar interactions such as  $\sigma_{\text{CH}} \rightarrow \sigma^*_{\text{CN}}$ ,  $\sigma_{\text{CH}} \rightarrow \sigma^*_{\text{CC(=O)}}$ ,  $\sigma_{\text{CC}} \rightarrow \sigma^*_{\text{CN}}$  and  $\sigma_{\text{CC}} \rightarrow \sigma^*_{\text{CC(=O)}}$ , atomic charges and the charge densities, the

overall relative acceptor ability of the three chosen functional groups is  $\text{NO}_2 > \text{NO} > \text{CHO}$ . Taking this into consideration and also the experimental observation that 3-CHO-cyclobutene opens exclusively inward, it is logical to expect that the corresponding better electron accepting  $\text{NO}_2$  and  $\text{NO}$  systems must also open inward.

In systems such as 3-substituted cyclobutenes,  $\sigma_{\text{C}_3\text{C}_4} \rightarrow \pi^*_{\text{NO}}$  and  $\sigma_{\text{C}_3\text{C}_4} \rightarrow \pi^*_{\text{CO}}$  interactions in the transition states leading to inward or outward opening of the ring are significant. These interactions are similar to  $\sigma_{\text{C}_1\text{H}} \rightarrow \pi^*_{\text{NO}}$  and  $\sigma_{\text{C}_1\text{H}} \rightarrow \pi^*_{\text{CO}}$  interactions present in  $\text{CH}_3\text{CH}_2\text{NO}$  and  $\text{CH}_3\text{CH}_2\text{CHO}$ , respectively. The more parallel the  $\sigma_{\text{C}_3\text{C}_4}$  and  $\pi_{\text{NO}}/\pi_{\text{CO}}$  orbitals, the better will be their interaction and, thus, the more facile the ring opening. Indeed, these interactions during the inward opening are much larger than in the outward opening for the three instances discussed herein.<sup>3</sup>

## ASSOCIATED CONTENT

### Supporting Information

Supporting Information (SI) available: Cartesian coordinates of the optimized ground state substrates studied at the MP2/cc-pVTZ//MP2/6-31G(d) level at 298.15 K.

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