Temporary Anions and Empty Level Structure in Cyclobutanediones: Through-Space and Through-Bond Interactions

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The energies of vertical electron attachment to cyclobutanone, its 2- and 3-oxa derivatives, 1,2-cyclobutanedione, and 2,2′,4,4′-tetramethyl-1,3-cyclobutanedione have been measured in the 0−6 eV energy range by means of electron transmission spectroscopy. The energies of temporary anion formation are nicely reproduced by shifting and scaling the virtual π^* orbital energies calculated for the MP2/6-31G*-optimized geometries of the neutral molecules. The linear correlation between experimental and calculated energy values reported in the literature for the empty π^*_{CC} orbitals fits the present data on the π^*_{CO} orbitals with the same accuracy. The two π^* anion states observed in the ET spectrum of the 1,3-dione (split by 1.25 eV) are assigned to the in-phase and out-of-phase combinations in order of increasing energy, i.e., the sequence dictated by through-space interaction. The calculations indicate a large through-space splitting (>2 eV) of the empty carbonyl π^* orbitals, reduced by through-bond destabilization of the in-phase combination.

Introduction

In gas-phase collisions, an isolated molecule can temporarily attach electrons of proper energy into vacant orbitals. This process gives rise to sharp variations of the total electron−molecule scattering cross section and is referred to as a resonance.[1] Electron transmission spectroscopy (ETS)[2] is one of the most suitable means for detecting the formation of these temporary anions. Because electron attachment is rapid with respect to nuclear motion, the anions are formed in the equilibrium geometry of the neutral molecule. The impact electron energies at which electron attachment occurs are properly denoted as vertical attachment energies (VAEs) and are the negative of the vertical electron affinities.

Within the Koopmans' theorem[3] (KT) approximation, VAEs are equal to the empty molecular orbital (MO) energies, just as the complementary ionization energies supplied by photoelectron spectroscopy are equal to the negative of the energies of the filled MOs. ETS has thus proved a powerful means for elucidating the empty level electronic structure and the mechanisms of interaction involving empty MOs.

The ET spectra of unsaturated hydrocarbons[5−7] indicated that through-space (TS) interactions among empty π^* orbitals are stronger than those in the corresponding filled counterparts. This finding was ascribed to the spatially more diffuse nature of the wave functions associated with empty orbitals. ETS has also shown that the net energy perturbation caused by methyl or CH_2 groups on adjacent π^* MOs is small,[5−7] indicating that the opposite effects of hyperconjugation with the pseudo-π filled σ_{CH} and empty σ^*_{CH} orbitals nearly balance each other. Only in small molecular π-systems, such as ethene or formaldehyde, does each replacement of a hydrogen atom with a methyl group produces a VAE increase of about 0.2 eV,[8] and similar effects are produced by the CH_2 group, as shown by the slight changes of the π^* VAE on going from 2-butene to cyclohexene[9] or from acetone to cyclohexanone.[10]

On this basis, the energy sequence expected for the in-phase (π_+^*) and out-of-phase (π_-^*) combinations of the ethene π^* MOs of 1,4-cyclohexadiene is that dictated by TS interaction, i.e., π_-^* above π_+^*. In contrast, by taking advantage of the different symmetry properties of the two MOs, the ET spectra of derivatives where the CH_2 groups are replaced with oxygen atoms or C=O groups,[11] and measurements of the angular electron scattering distributions,[12] it has been shown that the energy ordering is opposite.

A theoretical approach adequate for describing the energetics of temporary anion states involves difficulties not encountered for neutral or cation states. The KT approximation neglects correlation and relaxation effects, which tend to cancel out when ionization energies, but not electron affinities, are evaluated. Consistently, the calculated empty orbital energies overestimate the measured VAE by several electrovolts. However, the trends of the π^* MO eigenvalues of the neutral molecules supplied by Hartree−Fock (HF)/6-31G* calculations were found[13] to parallel the experimental VAEs, whereas inclusion of diffuse functions led to a breakdown in the correlation.[13,14]

The use of a finite basis set formed with Gaussian functions, owing to their radial rigidity and exponential decay, has the effect of confining the system in a box,[14] accounting in some way for the fact that during a resonance process the extra electron is confined to the molecule by a potential barrier. When the basis set is improved with diffuse functions, stabilization procedures are needed to distinguish the virtual orbitals which give rise to temporary anion states from those low-energy solutions having no physical significance with regard to the resonance process.[15,16]

The experimentally determined sequence and energy separation of the two π^* resonances of 1,4-cyclohexadiene were

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reproduced by KT-HF calculations using diffuse functions in conjunction with a stabilization procedure.[17−19] It was noticed,[19] however, that quite similar results are supplied by simple calculations (without a stabilization procedure) using a standard basis set not augmented with diffuse functions. All the theoretical approaches predicted a sizable TS splitting of the two empty ethene π^* orbitals, but an even larger through-bond (TB) destabilization of the MO (π_+^*) of proper symmetry, the latter effect being larger than expected on the basis of other ETS data (mentioned above).

In this work, ETS and theoretical calculations are employed to characterize the empty level structure of 2,2′,4,4′-tetramethyl-1,3-cyclobutanedione (**4**) and the related molecules cyclobutanone (**1**), 3-oxa-cyclobutan-1-one (**2**), 2-oxa-cyclobutanone (**3**), and 1,2-cyclobutanedione (**5**), the aim being to determine the energy ordering of the two π^* anion states and assess the extent of TS and TB interaction in the 1,3-dione. The empty π^* MO of the carbonyl group is largely localized at the carbon atom, and in the four-membered cyclo-1,3-dione, the distance between the carbonyl carbon atoms is smaller than that between the ethene groups in 1,4-cyclohexadiene. Thus, this molecular system would seem to be a suitable prototype for the study of TS interactions between nonbonded atoms.

Experimental Section

ET Spectra. Our electron transmission apparatus is in the format devised by Sanche and Schulz[2] and has been previously described.[20] To enhance the visibility of the sharp resonance structures, the impact energy of the electron beam is modulated with a small ac voltage, and the derivative of the electron current transmitted through the gas sample is measured directly by a synchronous lock-in amplifier. The present spectra were obtained by using the apparatus in the “high-rejection” mode[21] and are, therefore, related to the nearly total scattering cross section. The electron beam resolution was about 50 meV (fwhm). The energy scale was calibrated with reference to the $(1s^12s^2)^2S$ anion state of He. The estimated accuracy is ± 0.05 eV.

Computational Details. The calculations were performed with the Gaussian 98 set of programs.[22] Geometry optimizations on the neutral molecules are performed using the second-order many-body perturbation theory (MP2) and the 6-31G* basis set.[23]

The KT-HF virtual orbital energies of the neutral molecules were evaluated using the 6-31G* and the Dunning/Huzinaga valence double-ζ D95V[24] (C,O: 9s,5p/4s,2p; H: 4s/2s) basis sets, with the MP2/6-31G*-optimized geometries. The Gaussian primitives in the D95V basis set possess a more diffuse character compared to those in the 6-31G basis set and are a better choice in the description of anionic states. In particular, in a study[25] of the use of KT-HF calculations for the evaluation of π^* VAEs, as a function of basis set, the D95V empty MO energies calculated for the MP2/6-31G*-optimized geometries gave the best linear correlation with experiment.

Synthesis. 2,2′,4,4′-Tetramethyl-1,3-cyclobutanedione (**4**) and 1,2-cyclobutanedione (**5**) were prepared following literature procedures.[26,27]

Results and Discussion

Structural Parameters. The total energies of the most stable geometries of the neutral molecules were obtained with MP2 calculations using the 6-31G* basis set. For all compounds the results predict the conformation where the four atoms of the ring and the carbonyl oxygen atoms lie in the same plane to be the most stable, in agreement with gas-phase structural data available for **1**[28] and the 3-methyl derivative of **3**.[29] The C−C (1.553 Å) and C−C(O) (1.534 Å) bond lengths and the angle at the carbonyl group (92.70°) calculated in cyclobutanone (**1**) are in good agreement with the experimental values obtained with microwave and electron diffraction spectroscopy (C−C = 1.567[28] and 1.556 Å;[30] C−C(O) = 1.534[28] and 1.527 Å;[30] C−C(O)−C = 92.8°[28] and 93.1°[30]). The lengths of the C$=$O double bond calculated in cyclobutanone (1.214 Å) and formaldehyde (1.221 Å) are 0.01 Å larger than the corresponding experimental distances.[28,30]

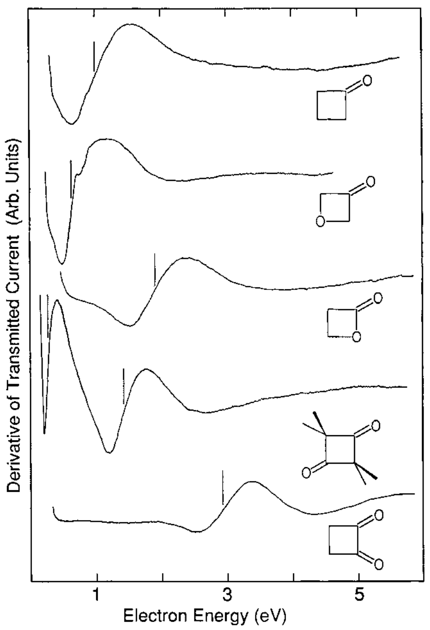

Figure 1. Derivative of the electron current transmitted through cyclobutanone (**1**), 3-oxa-cyclobutan-1-one (**2**), 2-oxa-cyclobutanone (**3**), 2,2′,4,4′-tetramethyl-1,3-cyclobutanedione (**4**), and 1,2-cyclobutanedione (**5**) as a function of the incident electron energy. Vertical lines locate the VAEs.

From the point of view of TS interaction, the most significant structural parameter is the distance between nonbonded carbonyl groups, which is predicted to be 2.111 and 2.092 Å, respectively, in 1,3-cyclobutanedione and in its tetramethyl derivative **4**. This distance is significantly shorter than that (2.500 Å[19]) between the ethene groups in 1,4-cyclohexadiene.

ET Spectra. Figure 1 reports the ET spectra of compounds **1**−**5**. The vertical lines locate the most probable VAEs, reported in the correlation diagram of Figure 2 and in Table 1. The π^* resonance of cyclobutanone is centered at 1.00 eV, to be compared with 1.15 and 1.30 eV measured in cyclopentanone and cyclohexanone,[10] respectively. The π^*_{CO} VAE thus gradually decreases with increasing ring strain.

In 3-oxa-cyclobutan-1-one (**2**), the CH_2 group opposite to the carbonyl group is replaced by an oxygen atom. The electron-withdrawing effect of oxygen is expected to stabilize the π^* anion state. In principle, however, this effect could be counteracted by (TS) charge-transfer interaction between the oxygen lone pair of π symmetry and the π^*_{CO} MO.[31] The π^* resonance of **2** displays two vibrational features spaced by 230 meV. The first and most intense feature is located at 0.61 eV. The 0.4 eV stabilization of the π^*_{CO} MO relative to cyclobutanone indicates that TS interaction with the oxygen lone pair (which would act in the opposite direction), if any, is small.

In 2-oxa-cyclobutanone (**3**), where the oxygen atom is adjacent to the carbonyl group, lone pair/π^* mixing causes a

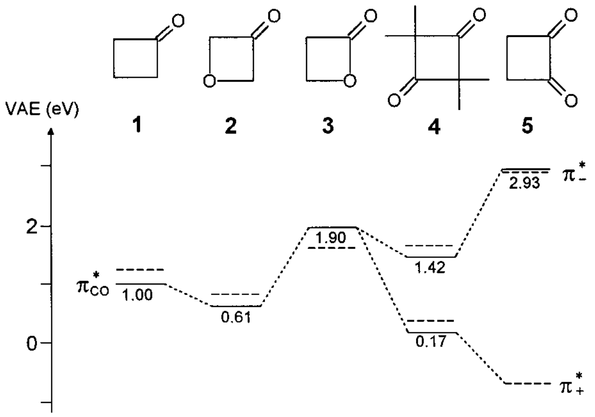

Figure 2. Diagram of the VAEs (full lines) measured in compounds **1**−**5**. The dashed lines represent the scaled VOEs (see text) obtained with the D95V basis set for the MP2/6-31G*- optimized geometries.

TABLE 1: Carbonyl π* MO Energies Calculated with the 6-31G* and D95V Basis Sets for MP2/6-31G*-Optimized Geometries, Scaled and Shifted Virtual Orbital Energies (in Parentheses − See Text), and Experimental Electron Attachment Energies. All Values in EV

compound	orbital	HF/6-31G*	HF/D95V	VAE
cyclobutanone (**1**)	π^*	3.81 (1.04)	3.59 (1.24)	1.00
	π	−12.86	−12.92	
3-oxa-cyclobutanone (**2**)	π^*	3.47 (0.82)	3.02 (0.82)	0.61
	π	−14.52	−14.21	
2-oxa-cyclobutanone (**3**)	π^*	4.64 (1.58)	4.05 (1.58)	1.90
	π	−15.37	−15.76	
2,2′,4,4′-tetramethyl-1,3-cyclobutanedione (**4**)	π_-^*	4.59 (1.54)	4.14 (1.65)	1.42
	π_+^*	2.87 (0.43)	2.46 (0.41)	0.17
	π_+	−13.04	−13.15	
	π_-	−14.03	−14.24	
1,3-cyclobutanedione	π_-^*	4.49 (1.48)	3.85 (1.43)	
	π_+^*	2.43 (0.14)	2.18 (0.20)	
	π_+	−13.56	−13.71	
	π_-	−14.63	−14.92	
1,2-cyclobutanedione (**5**)	π_-^*	6.35 (2.68)	5.81 (2.88)	2.93
	π_+^*	1.35 (−0.56)	0.97 (−0.69)	<0
	π_-	−13.66	−13.80	
	π_+	−15.01	−15.31	
formaldehyde	π^*	3.64 (0.93)	2.83 (0.68)	0.86[a]
	π	−14.28	−14.46	
distorted formaldehyde	π^*	4.08 (1.21)	3.15 (0.91)	
	π	−13.98	−14.31	
distorted formaldehyde dimer	π_-^*	5.32 (2.02)	4.56 (1.96)	
	π_+^*	2.29 (0.07)	1.49 (−0.31)	
	π_-	−14.06	−14.36	
	π_+	−14.47	−14.86	

[a] Taken from ref 32.

large net destabilization of the latter MO. The VAE of **3** is 0.90 eV higher than that of cyclobutanone, in line with the similar effect (0.81 eV) observed in the pentacyclic analogues.[10]

Because of the tautomeric instability of 1,3-cyclobutanedione, its tetramethyl derivative **4** was prepared and analyzed. The ET spectrum of **4** displays both the π^* resonances above zero energy, at 0.17 and 1.42 eV. Let us first consider the hypothesis that the two resonances are associated with the in-phase (π_+^*) and out-of-phase combinations (π_-^*) in order of increasing energy (i.e., the sequence dictated by TS interaction). Assuming that before TS and TB interactions the energy of the two π^* MOs is 0.5−0.6 eV (a few tenths of an eV lower than in formaldehyde, VAE = 0.86 eV[32]), owing to the mutual inductive effect exerted by the two carbonyl groups, the VAE (1.42 eV) of the π_-^* MO would lead to a TS splitting of 1.6−1.8 eV. The π_+^* MO, which can mix by symmetry with the σ_π MOs, would then be destabilized from about −0.3 eV to 0.17 eV. A TB destabilization of about 0.5 eV is consistent with the above-mentioned small-energy perturbations usually caused by alkyl groups on adjacent empty π^* MOs, given that the starting energy of the π_+^* MO is considerably lower than that of ethene or formaldehyde.

On the other hand, the reversed assignment of the two resonances (π_+^* above π_-^*) would imply a very strong inductive stabilization of the two π_{CO}^* MOs, a TS interaction which raises the energy of the π_-^* MO to 0.17 eV and a very large (1.2 eV larger than the TS splitting) TB destabilization of the π_+^* MO. This hypothesis is not in line with the effects observed in many other molecular systems, but it would parallel the energy ordering unambiguously demonstrated for 1,4-cyclohexadiene.

Finally, the ET spectrum of the 1,2-dione **5** displays a single resonance, located at 2.93 eV. Its assignment to the π_-^* MO, destabilized by strong mixing between the two adjacent carbonyl π^* orbitals, is straightforward. The π_+^* counterpart gives rise to a stable anion state, thus not detectable in ETS.

KT-HF MO Energies. In the study of the empty level structure of fused 1,4-cyclohexadiene rings,[19] it was noticed that the virtual orbital energies (VOEs) supplied by simple KT-HF calculations with the D95V basis set[24] (which does not include diffuse and polarization functions) match the experimental π^* VAEs substantially as well as the VOEs obtained with more sophisticated calculations, using a basis set improved with diffuse and polarization functions, in conjunction with an exponent stabilization procedure to distinguish the virtual MOs associated with temporary anion formation. With both methods, because of the neglect of correlation and relaxation effects, the π^* VOEs are generally 2−3 eV higher than the measured VAEs. In addition, this discrepancy increases with increasing energy, so that also the calculated energy gaps tend to be overestimated.

Staley and Strnad[25] correlated 56 experimental π^* VAEs of alkenes and benzenoid hydrocarbons with the corresponding VOEs supplied by simple KT-HF calculations using various basis sets. The shifted and scaled VOEs were found to be in good quantitative agreement with experiment. The best linear fitting (correlation coefficient = 0.99, largest absolute error = 0.32 eV) was obtained with the D95V VOEs calculated for the MP2/6-31G*-optimized geometries.

Table 1 reports the π^* VOEs obtained with the 6-31G* and D95V basis sets for the MP2/6-31G*-optimized geometries of the present cycloketones and formaldehyde. The VOEs shifted and scaled according to the linear regression given by Staley and Strnad[25] are reported in parentheses. Those obtained with the D95V basis set are also displayed as dashed lines in the diagram of Figure 2. The evaluated VAEs closely match experiment, the largest difference (0.32 eV) being found in **3**.

In 1,3-cyclobutanedione and its tetramethyl derivative **4**, the calculations confirm the above prediction, based on qualitative perturbational analysis, that the π_+^* MO lies at lower energy, that is, the energy ordering dictated by TS interaction. The scaled D95V VOEs and, in particular, the π_+^*/π_-^* energy splitting (1.24 eV, see Table 1) accurately reproduce the ET spectrum of **4**.

In **5** the scaled D95V VOE of the π_-^* MO is 2.88 eV (very close to the measured VAE), whereas the π_+^* anion state is predicted to be 0.69 eV more stable than the neutral state (positive electron affinity), in line with the absence of low-energy signals in the ET spectrum..

Table 1 also reports the energies calculated for the filled carbonyl π MOs. The neglect of correlation and relaxation effects tend to compensate when the ionization energies (IEs)

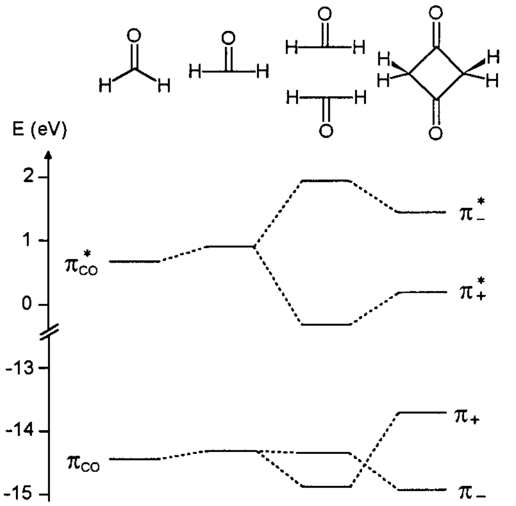

Figure 3. Diagram of the energies calculated (see text) for the filled and empty carbonyl π orbitals of formaldehyde, distorted formaldehyde and its dimer, and 1,3-cyclobutanedione.

are evaluated. As a result, the π MO energies (with opposite sign) usually reproduce satisfactorily the corresponding IEs. In the ketones, the calculated π_{CO} energies cannot be compared with experiment because ionization from the filled π_{CO} MOs occurs in the same energy range of the σ_{CC} and σ_{CH} MOs, so that the photoelectron spectra display a broad and unresolved signal. However, in formaldehyde the π_{CO} band is well resolved, and the measured vertical IE (14.5 eV[33]) is closely reproduced by the calculated energy (see Table 1).

It can be noticed that for the filled π_{CO} MOs of 1,3-cyclobutanedione and **4**, the calculations predict an energy sequence opposite to that of the empty π^* counterparts. In line with the expected large (TB) destabilization caused by mixing with the adjacent filled σ_π MOs, the in-phase π_+ MO lies 1.1−1.2 eV above the π_- MO (which cannot interact by symmetry).

To evaluate separately the TS and TB effects in the empty and filled π MOs, the calculations are extended to formaldehyde and to a formaldehyde dimer where the carbon atoms are placed at the same distance (2.111 Å) found for the MP2/6-31G* optimized geometry of 1,3-cyclobutanedione. In the dimer the bond lengths are kept equal to those of formaldehyde, but (to avoid repulsion between the hydrogen atoms) the H−C−H angle is opened to 180°. Distortion of the formaldehyde molecule leads to an increase of the total energy of 3.1 eV relative to that of the optimized geometry, whereas the total energy of the dimer is calculated to be 1.5 eV higher than that of two distorted monomers.

The calculated energies of the empty and filled π_{CO} MOs are given in Table 1. The diagram of Figure 3 reports the scaled π^* VOEs and the filled π MO energies obtained with the D95V basis set. A relatively small (0.2 eV, see Figure 3) destabilization of both the filled and empty π MOs occurs on going to formaldehyde to distorted formaldehyde. In the dimer (where TB interaction cannot occur) the empty π_-^* and π_+^* MOs and the filled counterparts are (TS) split by 2.27 and 0.5 eV, respectively. The relative magnitudes of the TS effect in the empty and filled orbitals are in line with the expectation of a larger overlap in the empty MOs because of their larger localization on the carbon atoms and a spatially more diffuse nature. Moreover, the present π_-^*/π_+^* TS interaction is particularly large (the 3.07 eV splitting of the nonscaled D95V VOEs is to be compared with the 1.63 eV splitting supplied by the same calculations in 1,4-cyclohexadiene[19]).

On going from the formaldehyde dimer to 1,3-cyclobutanedione, the π_-^*/π_+^* splitting is reduced from 2.27 to 1.23 eV (see Table 1 and Figure 3). The whole difference (1.0 eV) could be ascribed to TB destabilization of the π_+^* MO. On the other hand, only the destabilization of the π_+^* MO (0.5 eV) could be taken as a measure of the TB effect. It is to be noticed that the noninteracting empty and filled π_-^* and π_- MO are stabilized by 0.5 eV on going from the dimer to the dione. Only part of this effect (about 0.2 eV, as evaluated from formaldehyde and distorted formaldehyde) is due to reduction of the 180° bond angle at the carbonyl carbon atoms and is thus expected to affect also the π_+^* MO. An explanation for the remaining stabilization is not straightforward, but an analogous effect was found for the π_-^* and π_- MOs on going from the ethene dimer to 1,4-cyclohexadiene,[17,19] where it was ascribed to the variation of the localization properties of the in-phase counterparts upon mixing with the σ_π orbitals and consequent reduction of the screening effect exerted on the other MOs. Thus, an evaluation of 0.7−0.8 eV for the TB destabilization of the empty π_+^* MO seems to be reasonable.

On going from the dimer to 1,3-cyclobutanedione, the energy ordering of the filled π_- and π_+ MOs is reversed. The variation of their splitting is 1.7 eV, while the destabilization of the π_+^* MO is 1.15 eV. Considerations analogous to those made above for the empty MOs lead to a TB destabilization of about 1.4 eV for the filled π_+ MO.

Conclusions

Because of the relatively short distance between the two opposite vertexes of a cyclobutane ring and the large localization of the empty π_{CO}^* orbital of the carbonyl group on the carbon atom, 1,3-cyclobutanedione is a suitable molecular system to highlight through-space (TS) interactions. The empty level structure of cyclobutanone derivatives and cyclobutanediones has been characterized by means of electron transmission spectroscopy. KT-HF calculations with the D95V basis set (which does not include polarization and diffuse functions) have been used to evaluate the orbital energies for the MP2/6-31G* optimized geometries.

Previous work has demonstrated a very good linear correlation between the calculated virtual orbital energies and the π^* electron attachment energies measured in a large number of alkenes and benzenoid hydrocarbons. Here it is shown that the same equation can be successfully applied to evaluate the energies of carbonyl π^* anion states. The attachment energies measured in the ketones considered are reproduced with an average error of 0.2 eV.

The scaled virtual orbital energies accurately reproduce the experimental splitting between the energies of electron attachment to the two empty π^* orbitals of 1,3-cyclobutanedione and predict the energy sequence dictated by TS interaction, in contrast with the corresponding filled π orbitals. The energies calculated for a hypothetical formaldehyde dimer (where through-bond interaction cannot occur) indicate a large (2.3 eV) TS splitting of the empty carbonyl π^* orbitals, and a through-bond (TB) destabilization of about 0.7−0.8 eV of the (in-phase) lower-lying orbital in 1,3-cyclobutanedione. The magnitude of the latter effect is consistent with literature ETS data on the energy perturbations caused by alkyl groups on adjacent empty π_{CO}^* orbitals.

For the filled carbonyl π orbitals the calculations indicate a sizably smaller TS interaction (in agreement with their mainly oxygen character and the spatially less diffuse nature of the wave functions associated with filled orbitals) and a larger TB destabilization of the (in-phase) orbital of proper symmetry, in line with the energy proximity to the filled σ_π MOs.

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