

277. The Interaction of Nonbonding Orbitals in Carbonyls

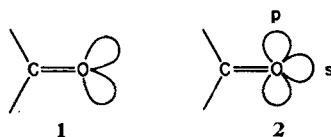
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Zusammenfassung. In Dicarbonylen wie Glyoxal oder Benzochinon bilden die nichtbindenden Sauerstofforbitale delokalisierte Molekelorbitale mit verschiedenen Energien. Wir berichten über EHT- und CNDO/2-Berechnungen einiger Dione und Trione. Die berechnete Aufspaltung zwischen den «nichtbindenden» Kombinationen wird auf der Grundlage der «through-space» und «through-bond» Wechselwirkung analysiert. Bei den tiefliegenden nichtbindenden Orbitalen der Carbonylgruppen scheint der zweite Faktor zu dominieren. Gerüst- σ -Orbitale und nichtbindende Sauerstofforbitale sind stark miteinander gemischt.

An isolated carbonyl group is characterized by two 'lone-pair' orbitals, described as equivalent in the valence structure 1. In any molecular orbital description of a carbonyl group, symmetry adapted combinations of these two equivalent lone-pairs must be taken, resulting in the s and p type lone-pairs of 2. The latter orbitals are



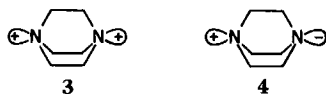
nonequivalent and possess widely differing energies. There is little doubt that the highest occupied σ molecular orbital of simple aldehydes and ketones is p type. It is this orbital which is most directly involved in (n, π^*) electronic transitions and in the mass spectral reactions of such compounds.

In molecules containing several equivalent carbonyl groups the 'nonbonding' p orbitals must be combined into more delocalized wave functions. These molecular orbitals, degenerate in the absence of any interaction, may as a result of interaction between the individual nonbonding orbitals be differentiated in energy. The energy splitting between these molecular orbitals is the prime operational measure of the extent of orbital interaction. Experimentally, this splitting may be obtained by ascertaining the ionization potentials of the appropriate orbitals. Through the technique of photoelectron spectroscopy [1] such measurements have become feasible.

Whenever nonbonding orbital interaction was considered in the past, that interaction was judged small¹⁾. This is now not in accord with either theoretical or experimental results. Lone-pairs, double bonds and other isolated subunits of a molecule interact significantly with other such units by direct through-space and indirect through-bond mechanisms. These interactions are easily analyzed [3] [4]. In particular we have had some success with an analysis of nitrogen lone-pair interactions. Thus in 1,4-diazabicyclo[2.2.2]octane we predicted a large gap of 1.57 eV

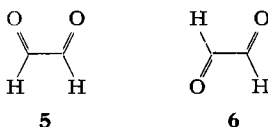
¹⁾ See for example the considerations for glyoxal and biacetyl in [2].

between the symmetric (**3**) and antisymmetric (**4**) lone-pair combinations [3]. An analysis of the through-bond coupling rationalized the apparent anomaly of the anti-

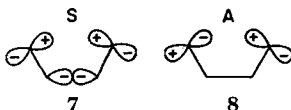


symmetric level appearing at lower energy. The large magnitude of the interaction has been confirmed, the corresponding experimental difference between the relevant ionization potentials being 2.11 eV [5]; more recently the energy ordering has been proven [6]. In this paper we present a theoretical analysis of the interaction of *p* type lone-pairs in dicarbonyl and tricarbonyl compounds. We have carried out approximate molecular orbital calculations of two types – CNDO/2 [7] and extended *Hückel* (EH) [8]²⁾ – on a series of dicarbonyls.

The first cases studied were *s-cis* and *s-trans* conformations of glyoxal, **5** and **6**. For the idealized geometries chosen³⁾ we obtained for both **5** and **6** an antisymmetric



(A) combination below a symmetric (S) molecular orbital⁴⁾. The energy gap between S and A was for **5**, 1.46 (EH) or 2.96 eV (CNDO), and for **6**, 1.46 (EH) or 3.27 eV (CNDO). The recently measured splitting is 1.6 eV [9]. The approximate form of the S and A combinations is shown in **7** and **8** below.



The explanation of the level ordering in terms of a through-bond coupling follows the arguments applied by us before for *para*-benzyne, pyrazine and diazabicyclo-

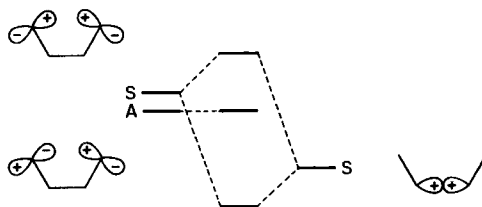


Fig. 1. Interaction diagram for the nonbonding oxygen orbitals and the C–C σ bond in *s-cis* glyoxal. The nonbonding orbitals, degenerate in energy before interaction, are slightly separated for greater clarity

²⁾ In our present calculations we have used a hydrogen Slater exponent of 1.3.

³⁾ All angles 120°, C–C 1.50 Å, C=O 1.22 Å, C–H 1.07 Å.

⁴⁾ The symmetry classification is with respect to the two-fold rotation axis in both **5** and **6**. In **5**, the orbitals have the same symmetry properties under reflection in the mirror plane bisecting the C–C bond as they do under the two-fold axis.

octane [3]. We consider the interaction of the S and A nonbonding orbital combinations with the C–C σ bond in Figure 1. Because the oxygen nonbonding orbitals are at low energy, we may assume that interaction with C–C σ^* is unimportant. The S nonbonding combination is clearly destabilized by this interaction.

We have assumed that the through-space interaction in *s-cis* glyoxal is small. This assertion is based on the magnitude of the overlap integral between two pure *p* type lone-pairs in our idealized geometry, that overlap amounting to only 0.011. An interesting numerical experiment designed to increase the rôle of the direct interaction was performed. We diminished both C–C–O angles symmetrically, thus bringing the two oxygen atoms closer to each other. The behavior of the two highest occupied levels in the molecule is shown in Fig. 2.

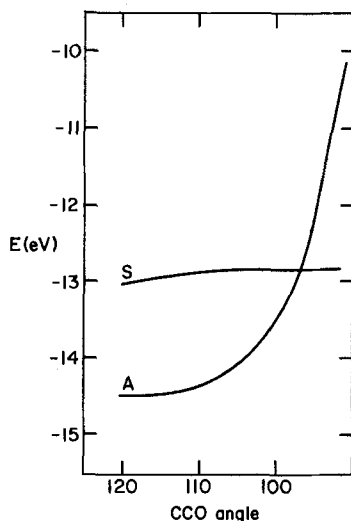


Fig. 2. Energy of two highest occupied molecular orbitals in glyoxal as a function of C–C–O angle

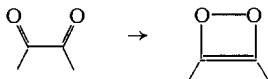
As the direct through-space coupling increases with smaller C–C–O angles we would expect the A level to move up, the S level to move down in energy. The A level follows this expectation, but the S level remains at approximately constant energy. We think that this is due to two competing effects: the energy-lowering direct overlap is balanced by an increased through-bond coupling. This is illustrated in Figure 3.



Fig. 3. Overlap of oxygen nonbonding orbitals with C–C σ bond in glyoxal for a large (left) and small (right) C–C–O angle

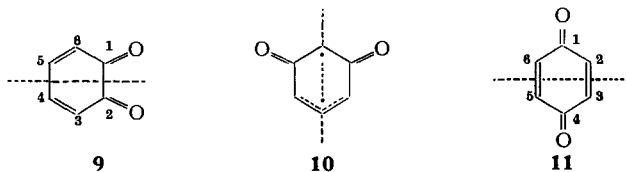
When the C–C–O angle is large, the overlap of either oxygen *p* orbital with an adjacent C–C σ bond is small – it is only the *p*–*p* π component of this overlap which is non-vanishing. When the C–C–O angle is 90° , this overlap is maximal.

It is amusing to note that near a C–C–O angle of 90° the rising A level crosses a low-lying π^* level. This level crossing is a manifestation of the forbiddenness of the reaction shown below.



The electronic spectrum of glyoxal has been studied in great detail. Electron diffraction [10] and infrared [11] studies on glyoxal have established that the ground state is *trans* planar, C_{2h} symmetry. Microwave studies [12] failed to reveal the presence of any *cis* or *gauche* isomers. The low frequency absorption spectrum of glyoxal exhibits a weak absorption near 5200 Å and a broad absorption beginning at 4550 Å [13]. The 5200 Å band was tentatively assigned by *Brand* [13] as a singlet-triplet transition. This assignment was confirmed by *Eberhardt & Renner* [14] in a study of the magnetic optical rotation spectrum of glyoxal. *King* [15] and *Paldus & Ramsay* [16] in rotational analyses of the 4550 Å absorption have shown unambiguously that the symmetry of the excited state is A_u and that the polarization of the transition is z (perpendicular to the molecular plane). Recently, the magnetic rotation spectrum of the 5200 Å band has been examined and shown to have a vibrational structure that is very similar to that of the singlet-singlet system [17]. The transition from the antisymmetric nonbonding orbital to the lowest π^* MO is forbidden, resulting in an excited state with B_g symmetry. The transition from the symmetric nonbonding MO is an allowed transition with z polarization, resulting in an excited state with A_u symmetry. Hence, our prediction that the symmetric combination of the nonbonding orbitals of glyoxal is of higher energy than the antisymmetric combination is consistent with the electronic spectrum of glyoxal. We might also mention here that the calculated EH splitting in norbornane-2,3-dione, a model rigid vicinal diketone, is 0.68 eV, with the antisymmetric combination being more stable.

We next studied the *ortho*-, *meta*- and *para*-benzoquinone, **9**, **10**, **11** respectively.



The results are summarized in the Table.

EH and CNDO Gaps between Symmetric and Antisymmetric Nonbonding Combinations

Molecule	Lower Level ^{a)}	Gap (eV)	
		EH	CNDO/2
<i>ortho</i> -benzoquinone	A	0.97	1.98
<i>meta</i> -benzoquinone	S	0.01	0.22
<i>para</i> -benzoquinone	S	0.47	1.92

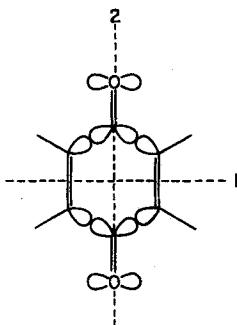
^{a)} Levels are specified as symmetric (S) or antisymmetric (A) with respect to the mirror plane shown in formulas **9**, **10**, **11**.

Note that the two procedures yield the same level ordering but that the splitting varied. There is at this time little experimental data available to evaluate our gap magnitudes. The photoelectron spectrum of *para*-benzoquinone has been reported [8], but the various ionization potentials were not assigned.

That the antisymmetric level in **9** is at lower energy is easily accounted for by a dominant through-bond interaction, analogous to that we analyzed above for glyoxal. The 1-2 σ bond is here also ideally aligned to interact with the p orbitals.

In some previous work [3] we reached the conclusion that through-bond coupling over any odd number of intervening σ bonds will place the antisymmetric combination $n_1 - n_2$ below the symmetric one $n_1 + n_2$. The *para*-benzoquinone **11** does not fit this rule. The generalization was based on the unique location of the central σ bond, allowing the destabilization of S by σ and the stabilization of A by σ^* . In **11** the bonds in question are the 2-3 and 5-6 σ bonds. Their overlap with the p type lone-pairs on oxygen is small, and so their rôle in coupling the lone-pairs cannot be large. Direct interaction, through-space, of the oxygen orbitals may be dismissed from consideration, since the oxygens are too far from each other. The rationale for the *para*-benzoquinone interaction pattern must be sought for in interactions which generate a significant overlap, in particular the interactions of the lone pairs with the 1-2, 1-6, 3-4 and 4-5 σ and σ^* levels.

Consider the interaction of the four σ bonds and the two lone-pairs⁵⁾.



From the p type lone-pairs we form the linear combinations of AA and SA symmetry. The four σ bonds give rise to SS, SA, AS and AA combinations, of these SA and AA interact with the lone-pair orbitals of the same symmetry. To allow the construction of an interaction diagram we need a relative energy ordering of the SA_σ and AA_σ levels relative to SA_p and AA_p . SA_σ would be expected to be at lower energy than AA_σ , since the former has fewer nodes. This is confirmed by an extended *Hückel* calculation on 1,4-cyclohexadiene (**12**), whose C-C σ skeleton is similar to that of **11**, and whose SA and AA orbitals would in particular be expected to resemble

⁵⁾ We find that we need not concern ourselves with the C-C σ^* levels, since the oxygen lone-pairs are at relatively low energy, much closer to the C-C σ levels.

those of **11**, since the second plane of symmetry passes through the atoms which make **11** different from **12**.



In an extended *Hückel* calculation an oxygen $2p$ orbital is bound about as much as a C–C σ level, and in fact the SA_σ and AA_σ levels are placed at higher energy than SA_p and AA_p . The important portion of the completed interaction diagram is shown in Figure 4. The higher occupied molecular orbitals are expected to be mixtures of σ and p orbitals, with each type of orbital contributing heavily. The isolated lone-pair

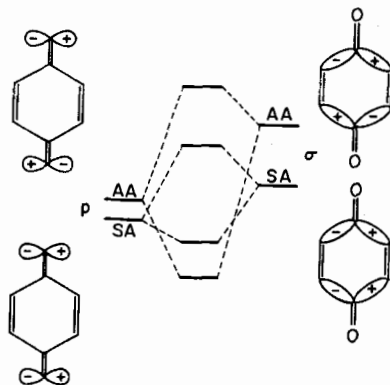


Fig. 4. Interaction diagram for para-benzoquinone

The oxygen nonbonding combinations SA_p and AA_p are at left, the carbon σ framework orbitals AA_σ and SA_σ are at right. The nonbonding orbitals, degenerate in energy before interaction, are slightly separated for greater clarity.

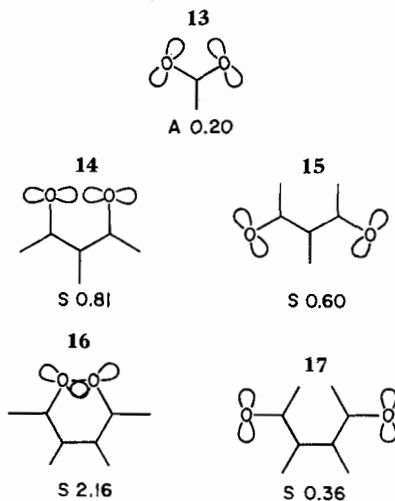


Fig. 5. Lone-pair interactions in some dicarbonyls

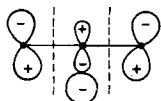
S indicates that the symmetric level is at lower energy. The number next to S is the energy splitting, in eV, between S and A

concept thus breaks down⁶⁾. The highest occupied AA level is 24% (EH) or 32% (CNDO) on both oxygens, and the SA level below it is 39% (EH) or 70% (CNDO) localized.

Figure 5 shows the extended *Hückel* results for some further model dicarbonyl compounds, differing in the number of intervening σ bonds.

The splitting between the nonbonding orbitals in the formate ion (**13**) is 0.20 eV for an O–C–O angle of 120°, with the antisymmetric combination at lower energy. *Ab initio* calculations on the same molecule yielded an identical level ordering, with splitting magnitudes of 0.10 [20] and 0.06 [21] eV. The level ordering is somewhat surprising, since one might have expected a direct interaction to place the symmetric combination at lower energy. When we examined the splitting as a function of O–C–O angle, we indeed found, analogous to the case of glyoxal discussed above, that at small O–C–O angles the symmetric combination moved to lower energy. S and A levels crossed at an O–C–O angle of approximately 116°. Very similar observations were made in the *ab initio* calculations [20] [21].

The dominant through-space interaction is clearly responsible for the level ordering at small O–C–O angles. Positioning of the A level at lower energy for large O–C–O angles may be rationalized in two ways, both suggested by the final shape of the destabilized S combination, illustrated schematically below for an O–C–O angle of 180°.

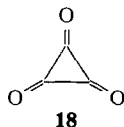


First we may think of the S and A combinations as being derived from protonation of a linear CO₂. It is then clear that whilst A is derived from the second allylic orbital of CO₂, S is descended from the uppermost (unfilled) allylic orbital of CO₂, and thus should be at higher energy. Alternatively we may consider interaction of the oxygen lone-pairs with the C–H σ and σ^* orbitals. Only the S combination may interact with these, and since in calculations with overlap included the σ^* levels are normally found to be more antibonding than the σ levels are bonding, we would expect a greater interaction, and consequent destabilization, of S with σ rather than with σ^* [3]. This is in accord with the nodal structure of the orbital shown above.

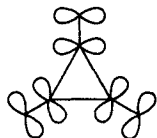
The level ordering in compounds **14** and **15** is primarily due to through-bond interaction mediated by the carbon skeletal σ bonds. At first one might have expected a large through-space interaction in **14**, since the oxygen *p* orbitals are optimally aligned for direct interaction. However the oxygen atoms are 2.60 Å apart and the 2*p* orbitals are quite contracted. The *p*–*p* σ overlap is only 0.017 and so the direct mixing, favouring the S combination, is a minor part of the entire interaction. In compound **17** the analysis follows that applied to *para*-benzoquinone. In the conformation **16** a large direct interaction is superimposed.

⁶⁾ We have never thought of the spectroscopic oxygen lone-pairs as being highly localized on oxygen. They are ideally oriented for interaction with the σ system of a molecule. In formaldehyde the best *ab initio* calculations show that the highest occupied MO is 75% localized on oxygen [18]. A striking experimental demonstration of lone-pair delocalization is the 2 eV difference in the first ionization potentials of acetone and hexafluoroacetone [19].

The hypothetical cyclopropane-trione (**18**) has a large calculated splitting of 2.72 eV with an a'_2 level below a degenerate e' pair.



Through-space overlap would place a'_2 above e' in a manner analogous to the interaction of double bonds in barrelene [4]. The *Walsh* orbitals of cyclopropane [22] are ideally oriented for π -type interaction with the oxygen nonbonding electrons. The interaction diagram parallels that given by us for bullvalene [4] and accounts for the large reversed splitting.



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