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Electronic Structure of Dicarbonyls. The Ground State of Glyoxal[1a]

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Abstract: The ground electronic state of the simplest α-dicarbonyl, glyoxal, $(CHO)_2$, has been studied by ab initio self-consistent field (SCF) methods using a double-ζ basis set of contracted Gaussian functions. The internal rotation potential curve was determined by optimizing the five structural parameters in the cis and trans forms and three intermediate geometries. The cis-trans energy separation was found to be 5.9 kcal/mol with the trans being the lower form. The internal rotation barrier was 7.5 kcal/mol with respect to the trans minimum, and the potential maximum occurs at an angle of about 102° away from the trans planar form. The energy ordering of the highest occupied molecular orbitals was determined to be n, π, n, and π, in order of increasing Koopmans theorem ionization potential. The close correspondence of these orbitals with those of two interacting CO molecules made possible generalizations of ground electronic state structure of α-dicarbonyls and some predictions concerning excited electronic states.

The reactivity, photochemistry, photophysics, and other properties of carbonyl-containing molecules have made them the subject of a wide variety of experimental studies. It is clear that such properties are intrinsically related to molecular electronic structure. Of particular interest in large or complex systems is determining the effect of localized CO electronic structure so as to facilitate prediction of the chemistry or properties of such systems. With existing theoretical descriptions of the electronic structures of simple carbonyl molecules, such as carbon monoxide[2-8] and formaldehyde,[9-16] a direct approach to this problem would be the theoretical study of a series of systems of more than one carbonyl. And an obvious beginning point is the simplest dicarbonyl, glyoxal.

Glyoxal has been an interesting molecule in photochemistry and spectroscopic studies since the early photolysis experiments of Norrish and Griffiths.[17] Their work and that of others[18,19] showed the dissociation products of glyoxal to be CO, formaldehyde, and hydrogen molecules. While the production of formaldehyde involves excited electronic states,[20,21] it appears hydrogen is formed from vibrationally excited ground electronic state molecules.[22] Spectroscopic work has shown the structure of the major form of glyoxal to be planar trans.[23,24] In 1970, *cis*-glyoxal was identified by high-resolution visible spectroscopy[25,26] and its planar structure was confirmed by microwave experiments.[27] No gauche forms have been detected.

The structure and properties of glyoxal depend largely on the valence molecular orbitals (MO's). Within the paradigm of carbonyl chemistry, these are expected to correlate with oxygen nonbonding orbitals and CO π orbitals. Since only a few excited states of glyoxal have been identified,[23,24,26,28] photoelectron spectroscopy along with semiempirical and ab initio calculations have been used to study the valence molecular orbitals. However, the results have not been entirely consistent.

Turner's assignment of the photoelectron spectrum of glyoxal[29] ordered the valence molecular orbitals as n_a, n_b, π_b, and π_a in order of increasing ionization potential (a and b subscripts denote C_2 rotational symmetry). The spectra also indicated the level separations were of about the same magnitude. This seems in agreement with CNDO calculations[30] showing the n_a-n_b splitting of otherwise degenerate noninteracting orbitals to be due to a through-bond interaction with the carbons. The acceptance of this description of the valence molecular orbitals has limited the search for excited states to n → π^* excitations, with the $\pi \rightarrow \pi^*$ states presumed to be much higher in energy. Qualitative interpretations concerning the O-C-C-O skeleton of biacetyl[31] and CNDO/CI calculations[32,33] of α-dicarbonyls have given generally the same ordering with some differences in the n_a-n_b separation. Also, minimum basis ab initio calculations[34] on the negative ion, $(CHO)_2^-$, have agreed with this ordering, though with some σ MO's located energetically among the n and π MO's.

The first work inconsistent with this MO scheme was the semi-empirical study of Kato et al.[35] They found the valence molecular orbitals to be ordered n_a, π_b, n_b, σ_a, π_a in the trans form and n_a, π_a, n_b, σ_a, π_b in the cis form. The separation of the highest π and lowest n for both forms

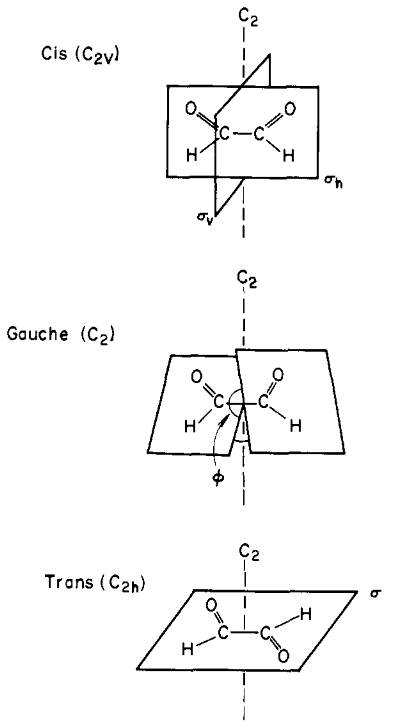

Figure 1. Glyoxal geometries.

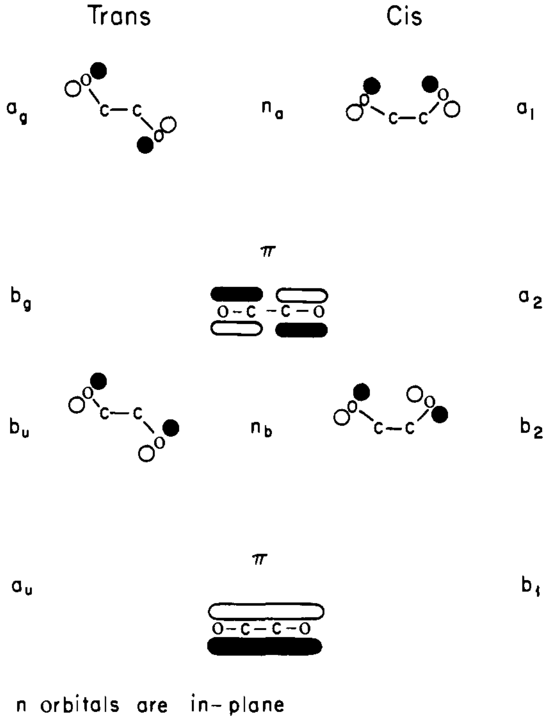

Figure 2. Qualitative representation of glyoxal n and π molecular orbitals. The combination of carbon and oxygen atomic p orbitals produces n and π orbitals localized on each CO. In a planar dicarbonyl, the π degeneracy is lost and the perpendicular components combine in phase or with opposite phase as indicated by the shading.

tended to be smaller than the other level separations. The important implications of this was seen in their prediction that $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ excited states would not be completely apart energetically. Pincelli et al.[36] used a double-ζ basis in an ab initio calculation on the ground state. They found an ordering of valence MO's similar to that of Kato, but with the highest σ MO's being lower than the n and π MO's. And a more recent calculation[37] with a less than double-ζ basis seems to agree, assuming that the symmetry designations presented should be interchanged.

Ab initio calculations[36-39] have been limited to the ground state. All have sought to determine the internal rotation barrier and the cis-trans separation, but the results have disagreed by as much as a factor of 2. This may be due to both the use of different basis sets and to different treatments of the geometry. Only one of these calculations[39] involved optimization of the geometry, which Dunning and Winter have demonstrated to be potentially important in internal rotation problems.[40]

The persistent electronic structure problem, then, is the determination of the nature of the highest filled molecular orbitals. A careful study of the ground state of glyoxal, including the internal rotation potential, and comparison with the interaction of two CO molecules may resolve this problem and improve understanding of dicarbonyl excited states.

Theoretical Approach

A double-ζ basis set of Dunning-contracted Gaussian functions[41] was used in all calculations: C (9s5p/4s2p), O (9s5p/4s2p), H (4s/2s). The quality of this basis set in LCAO-MO-SCF calculations has been reviewed elsewhere.[42]

However, we should note specifically that polarization functions (excluded here) are sometimes required to obtain quantitatively reliable potential curves for internal rotation. A particularly striking example is the work of Dunning and Winter[40] on hydrogen peroxide.

The five independent structural parameters in glyoxal are the carbon-carbon, carbon-oxygen, and carbon-hydrogen bond distances, and the carbon-carbon-oxygen and carbon-carbon-hydrogen bond angles. The gas-phase electron diffraction values of these parameters[43] for *trans*-glyoxal were used as a guess of the SCF optimum geometry. The parameters were varied iteratively and a simple parabolic fit of the molecular energy was used to predict the minimum with respect to the given parameter. The size of the variations was reduced after one cycle through all the parameters, and the process continued until the change in both the parameters and the energy became reasonably small. In all cases, the internal rotation angle, ϕ, was held fixed. Tests were made with other starting geometries to ensure that the iterative method had not converged to a local minimum. The optimization was performed for the trans ($\phi = 0°$), cis ($\phi = 180°$), and three gauche forms: $\phi = 45, 90, 135°$.

The symmetry representations of the molecular orbitals were an obviously important consideration. Glyoxal is a 30-electron system with a closed shell ground state. The molecular symmetry is C_{2h} in trans, C_{2v} in cis, and C_2 for the gauche forms. The three forms are illustrated in Figure 1. It can be seen that the C_2 rotation axis is in the molecular plane of the cis form, but perpendicular to the trans molecular plane. To check previous determinations of the orbital occupancies, SCF calculations were first performed in the reduced symmetry, C_2, on the cis and trans forms. The resulting molecular orbitals could then be identified with full symmetry representations.

As shown in Figure 2, oxygen nonbonding 2p atomic orbitals are combined symmetrically and antisymmetrically in order to transform as point group representations. This yields a_g and b_u in trans and a_1 and b_2 in cis, and like σ MO's they are clearly in the molecular plane. The π MO's are formed from atomic p orbitals perpendicular to the molecular plane and thus transform as a_u and b_g in trans and a_2 and b_1 in cis. The n and π descriptions are not appropri-

Table I. Glyoxal Ground State Energies

	Trans energy, hartrees	Cis/trans separation, kcal/mol	Barrier, kcal/mol
This work	−226.5182	5.9	7.5
Pincelli et al.[a]	−226.4703	6.4	7.9
Sundberg et al.[b]	−226.3246	4.8	7.2
Ha[c]	−226.2477	3.0	6.2
Radom et al.[d]	−226.2428	6.1	7.9

[a] Reference 36. [b] Reference 39. [c] Reference 37. [d] Reference 38; barrier is taken from the ϕ = 120° potential.

Table II. Glyoxal Geometry Optimization[a]

	ϕ, deg	R_{CC}	R_{CO}	R_{CH}	∠CCO	∠CCH	Energy,[b] hartrees
Trans	0	1.508	1.215	1.085	121.1	116.0	0.0
	45	1.509	1.215	1.085	121.4	116.0	0.0053
	90	1.512	1.215	1.085	122.7	116.0	0.0116
	102	Potential maximum[c]					0.0119
	135	1.514	1.214	1.085	123.1	115.5	0.0107
Cis	180	1.516	1.213	1.085	123.2	115.3	0.0094

[a] Bond distances are in Å, and bond angles are in degrees. [b] Energy is relative to trans. [c] Determined from potential curve.

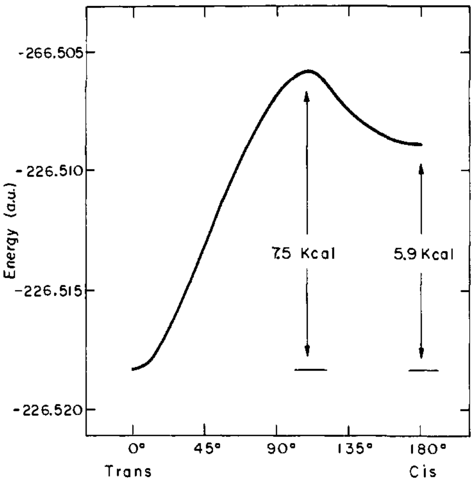

Figure 3. Internal rotation potential curve.

Table III. Dipole Moments (D)

	ϕ, deg	μ
Trans	0	0.0
	45	2.03
	90	3.66
	135	4.55
Cis	180	4.79
Cis[a]		4.8

[a] Microwave experimental result, ref 27.

ate in the reduced symmetry of the gauche structures. Since no p functions were used in the hydrogen basis, the π MO's are completely localized on the O–C–C–O skeleton and correlate directly with individual carbon monoxide MO's.

Results and Discussion

The double-ζ basis set and geometry optimization yielded an energy for *trans*-glyoxal lower than any previous calculation, as shown in Table I. The structural parameters for the optimized geometries are given in Table II. While all the changes were small, an increase in the C–C bond length and a decrease in the C–O bond length in going from trans to cis were found. Also, the C–C–O bond angle was found to be about 2.1° larger in the cis form than in the trans. This compares with experimental values of about 2.7[27] and 3°.[44] The C–H bond length was essentially the same in all structures.

The internal rotation barrier was calculated by a standard fit to a cosine series potential function and was found to be 7.5 kcal/mol at an internal rotation angle of 102°. The potential is shown in Figure 3. The energy difference between the cis and trans forms was 0.0094 hartree or 5.9 kcal/mol. Both values are within the range of previous calculations. The major disagreement is with the calculation of Ha[37] who used a near double-ζ atomic basis with assumed geometries, and obtained only 3.0 kcal/mol for the cis–trans separation. Ha's result is probably due to a choice of geometry far from the optimum. Indeed, the energy obtained by Ha with the near-double-ζ basis is about as good as that of Pople and coworkers[38] who used a smaller 4-31G basis.

Sundberg and Cheung used a somewhat less than double-ζ basis and performed a partial geometry optimization.[39] Specifically for the gauche forms they did not optimize the carbon–hydrogen and carbon–oxygen bond lengths and the carbon–carbon–hydrogen angle. While qualitatively they show a C–C bond length increase and a C–O bond length decrease, their C–C lengths are overall longer than determined in this work, and C–O lengths are shorter. Furthermore, their reported change between cis and trans in the CCO angle is smaller and less in line with experimental values.[27,44] A possible reason for these differences is that they used a larger set of primitives on oxygen than on carbon. Finally, though the change in the C–C–H bond angle is small, it is opposite in direction from our results. All of these geometry effects may be the result of their use of a less complete basis than our double-ζ set. The same considerations might explain their somewhat small cis-trans separation energy.

A double-ζ set was used by Pincelli and coworkers in an earlier calculation.[36] However, no geometry optimization was attempted, and we attribute part of the improvement in the total molecular energy over their result to the optimization. It seems that because the structural changes upon internal rotation are small, the barrier and separation results of the double-ζ calculation of Pincelli et al. are in qualitative agreement with the present work.

Experimental studies of the internal rotation potential have been limited. Currie and Ramsay used the difficult technique of following the temperature dependence of absorption intensity of vibrational bands in the visible absorption spectrum.[26] They reported the cis–trans energy difference to be 1125 cm^{-1} or 3.2 kcal/mol. More recently, Durig and coworkers presented an internal rotation potential with a barrier of about 4.6 kcal/mol,[27] but the determination of their potential explicitly used the cis–trans separation energy of Currie and Ramsay. Before the existence of *cis*-glyoxal was known, Fately and coworkers estimated a potential barrier of 13.7 kcal/mol using infrared frequencies of torsional vibrations in *trans*-glyoxal.[45] The inherent difficulties of both of the independent experimental approaches would suggest only that the true value may be somewhere between.

The change in the dipole moment upon internal rotation is shown by the calculated values at the five optimized geometries, as shown in Table III. Symmetry requires the dipole moment of *trans*-glyoxal to be identically zero. The calculated value of 4.79 D for the cis form agrees fortuitously well with the microwave spectroscopy value of 4.8 D.[27]

The nature of the ground state internal rotation potential may be important in the ground state dissociation of glyox-

Table IV. Glyoxal Orbital Energies in Hartrees[a]

Trans		Gauche				Cis	
Molecular orbital	$\epsilon_{0°}$	Molecular orbital	$\epsilon_{45°}$	$\epsilon_{90°}$	$\epsilon_{135°}$	Molecular orbital	$\epsilon_{180°}$
$5b_u\ \sigma$	−0.7076	5b	−0.7025	−0.6890	−0.6717	$6a_1\ \sigma$	−0.6802
$6a_g\ \sigma$	−0.6580	6a	−0.6665	−0.6735	−0.6779	$5b_2\ \sigma$	−0.6593
$1a_u\ \pi_a$	−0.6041	7a	−0.5853	−0.5548	−0.5325	$1b_1\ \pi_b$	−0.5981
$6b_u\ n_b$	−0.5349	6b	−0.5366	−0.5536	−0.5805	$6b_2\ n_b$	−0.5253
$1b_g\ \pi_b$	−0.5305	7b	−0.5351	−0.5358	−0.5304	$1a_2\ \pi_a$	−0.5239
$7a_g\ n_a$	−0.4484	8a	−0.4440	−0.4387	−0.4414	$7a_1\ n_a$	−0.4456

[a] These are the highest occupied molecular orbitals in the ground state.

Table V. CO–CO Interaction and Orbital Energies[a]

		R_{C-C} =					
		R_{opt}[c]	4.0	5.0	7.0	10.0	30.0
Energy		−225.1697	−225.3048	−225.3388	−225.3480	−225.3480	−225.3481
Cis	$5a_1\ \sigma$	−0.7375	−0.6738	−0.6340	−0.6180	−0.6156	−0.6142
	$5b_2\ \sigma$	−0.6045	−0.6097	−0.6134	−0.6158	−0.6155	−0.6142
	$1b_1\ \pi$	−0.6549	−0.6260	−0.6206	−0.6170	−0.6155	−0.6142
	$1a_2\ \pi$	−0.6010	−0.6132	−0.6168	−0.6166	−0.6155	−0.6142
	$6a_1$ n	−0.6583	−0.6140	−0.5933	−0.5690	−0.5622	−0.5604
	$6b_2$ n	−0.3643	−0.4774	−0.5270	−0.5576	−0.5617	−0.5604
Energy		−225.2582	−225.3229	−225.3455	−225.3487	−225.3503	−225.3503
Trans	$5a_g\ \sigma$	−0.7201	−0.6733	−0.6322	−0.6173	−0.6168	−0.6161
	$5b_u\ \sigma$	−0.6673	−0.6267	−0.6179	−0.6158	−0.6167	−0.6161
	$1a_u\ \pi$	−0.6409	−0.6234	−0.6199	−0.6167	−0.6167	−0.6161
	$1b_g\ \pi$	−0.5822	−0.6109	−0.6162	−0.6163	−0.6167	−0.6161
	$6a_g$ n	−0.6021	−0.5995	−0.5910	−0.5692	−0.5621	−0.5601
	$6b_u$ n	−0.4149	−0.4900	−0.5318	−0.5584	−0.5617	−0.5601

[a] Geometries were analogous to glyoxal optimized structures with only R_{C-C} being varied. [b] The carbon–carbon separation is in bohrs and energies are in hartrees. [b] The 30.0 bohr cis and trans energies differ because R_{C-O} is different in optimized *cis*- and *trans*-glyoxal. [c] R_{opt} is the carbon–carbon optimized bond length in *cis*- or *trans*-glyoxal.

al. In 1964, Parmenter used quantum yield studies to show that vibrationally excited ground electronic state molecules could dissociate to produce hydrogen and carbon monoxide.[22]

$$(CHO)_2^* \rightarrow H_2 + 2CO$$

Parmenter estimated that $(CHO)_2^*$ must be formed with about 55 kcal/mol of internal energy in his experiments. Since this is much greater than the 7.5 kcal/mol trans-cis barrier in glyoxal, and isomers could easily interconvert, we were interested in the possible isomer preference of the dissociation. A comparison of the energies of *cis*- and *trans*-glyoxal at seven C-C distances (other parameters at their optimum) covering a range of 0.17 Å around each minima showed the cis potential to be only slightly shallower than the trans potential. A small difference is expected because, relative to the dissociation products, the trans form is lower than the cis by the 5.9 kcal/mol separation energy. Finding no large differences in the two C-C potentials, it seems that even at much larger separations this type of comparison may be too insensitive to demonstrate what is probably at most a small isomer preference. However, it is interesting to note that if the dissociation is unimolecular, formation of H_2 might be favored in the cis form because the hydrogen atoms are spatially much closer.

Electronic Structure Considerations

The electronic structures of glyoxal and CO-CO are characterized by the valence orbital energies, Mulliken populations, and the orbital eigenvectors. Orbital energies are given in Tables IV and V and are plotted in Figures 4 and 5. The first interesting feature is that the n and π MO's are not completely separate energetically and, in fact, the ordering is n, π, n, and π. Also, the π_a and π_b MO's, while about 0.074 hartree apart in both the cis and trans forms, reverse their order between the forms. And because only a and b symmetry is maintained in the gauche forms, the trans π_b necessarily correlates with the cis n_b. The trans n_b becomes the cis π_b.

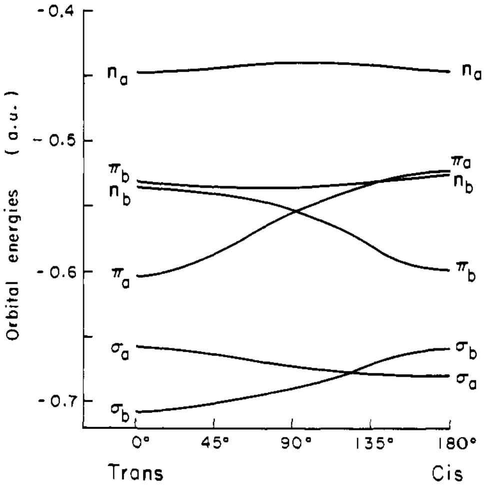

Figure 4. Glyoxal orbital energies. Because of the reduction to C_2 symmetry in the gauche forms, the n and π designations are inappropriate for other than the planar forms. The reduction in symmetry also makes possible the correlation of cis n orbitals with trans π orbitals, etc.

The Mulliken populations given in Table VI demonstrate the atomic character of the valence MO's. The oxygen p atomic orbitals (AO's) form the n_b orbital almost exclusive of contributions from any other center. However, hydrogen and carbon do participate in the n_a MO. The trans π_b and cis π_a, which are the highest π's energetically, have a node

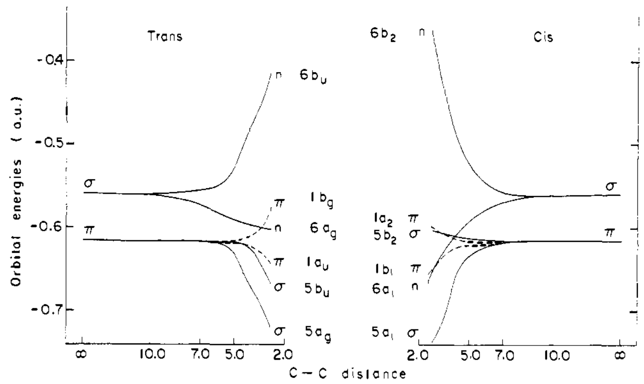

Figure 5. Interaction of two CO molecules. The breakdown of localized n and π molecular orbital symmetry is indicated by the plots of orbital energies with varying CO–CO distance. The CO molecules were held in a planar arrangement, either cis or trans, with the C–C–O angle and C–O bond length being those of the analogous optimized cis or trans glyoxal structures.

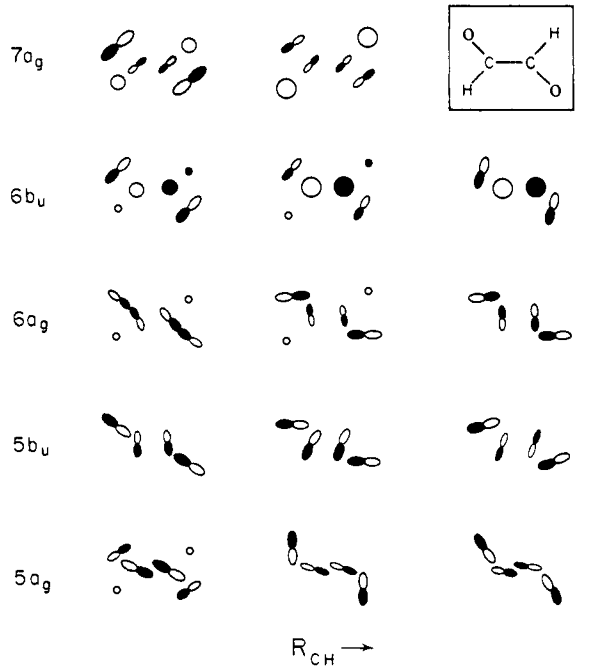

Figure 6. Valence orbital representations. Molecular orbitals are represented by the most important atomic orbitals in the MO eigenvector. Size of each orbital corresponds roughly to the eigenvector coefficient. Shading is used to designate phases. The left most orbitals are for the optimum *trans*-glyoxal geometry. The next two sets are at carbon-hydrogen distances of 2.5 and 6.0 Å (as in Table VII).

between the carbons (see Figure 2). Thus, the oxygen p contribution to these MO's dominates the carbon p contribution. In the other π MO's, there is no node and the carbon p population is more nearly equivalent.

The MO's which result from the interaction of two CO molecules have some similarity to glyoxal MO's. As shown in Figure 5, the degeneracy of the σ and π MO's of the two separate carbon monoxide molecules is lost by the interaction at distances of about 7 bohrs or less. In C_{2h} or C_{2v} symmetry, the oxygen p AO's directed along the C–O axis can mix with oxygen p AO's perpendicular to the axis but in the CO–CO plane. As a result, the individual highest filled σ MO's of CO correlate with n orbitals in CO–CO. The components of the carbon monoxide π MO's become π CO–CO MO's and σ-like low-lying molecular orbitals.

In their CNDO study of dicarbonyls,[30] Swenson and Hoffmann demonstrated that the interaction which removes the n orbital degeneracy in glyoxal is a through-bond interaction with the carbons, and specifically, they believed, through the carbon 2p orbitals directed along the C–C axis. In addition, we find from a detailed examination of the orbitals that the interaction involves carbon 2p orbitals perpendicular to the axis to facilitate delocalization of the n electrons on the hydrogens in the n_a MO. In the n_b MO the carbon 2s orbitals are important. To better understand the n electron delocalization, we have performed four test calculations on the trans ground state of glyoxal by slowly increasing the carbon–hydrogen distance. The results are given in Table VII. At R_{CH} = 6.0 Å, the system resembles *trans*-CO–CO with an additional orbital ($7a_g$) for the hydrogen electrons. (See footnote *b* to Table VII for a more realistic description of these two electrons.) The Mulliken populations show how the $6a_g$ becomes n type in CO–CO. Surprisingly, the $6b_u$ orbital loses much of its localized oxygen character. Furthermore, the n_b ($6b_u$) MO of CO–CO is *higher* than the n_a ($6a_g$) MO. This reversal in n_a–n_b ordering demonstrates the importance of n electron delocalization. If the through-bond interaction which removes the n degeneracy were only via carbon 2p AO's along the C–C axis, the interaction should be largely independent of the presence of hydrogens. Thus, taking the conclusions of

Table VI. Mulliken Populations[a]

		n_a	π_b	n_b	π_a
		trans-Glyoxal			
Oxygen	s	0.000		0.000	
	p	0.630	0.732	0.818	0.536
Carbon	s	0.004		0.049	
	p	0.192	0.267	0.043	0.464
Hydrogen	s	0.174		0.090	
		cis-Glyoxal			
Oxygen	s	0.000		0.002	
	p	0.639	0.526	0.820	0.713
Carbon	s	0.005		0.046	
	p	0.185	0.474	0.040	0.287
Hydrogen	s	0.171		0.092	

[a] The Mulliken populations for valence glyoxal molecular orbitals are shown broken down in atomic orbital types. The values are for one of the two equivalent centers: oxygen, carbon, or hydrogen.

Table VII. Removal of Hydrogens from *trans*-Glyoxal[a]

		R_{CH} =				
		R_{opt}	1.35	2.5	4.2	6.0
		Orbital Energies				
ϵ ($7a_g$)[b]		-0.4493	-0.4369	-0.3175	-0.2316	-0.2196
($6b_u$)		-0.5347	-0.5183	-0.4188	-0.4167	-0.4176
($6a_g$)		-0.6577	-0.6365	-0.5922	-0.5957	-0.5985
($5b_u$)		-0.7076	-0.7050	-0.6630	-0.6643	-0.6664
		Mulliken Populations				
$7a_g$	Oxygen	0.630	0.496	0.098	0.0	0.0
	Hydrogen	0.174	0.280	0.666	0.992	1.000
$6b_u$	Oxygen	0.818	0.692	0.320	0.350	0.344
	Hydrogen	0.090	0.154	0.206	0.0	0.0
$6a_g$	Oxygen	0.634	0.514	0.716	0.729	0.728
	Hydrogen	0.112	0.156	0.012	0.0	0.0
$5b_u$	Oxygen	0.745	0.641	0.620	0.611	0.617
	Hydrogen	0.023	0.061	0.015	0.0	0.0

[a] Carbon–hydrogen distances are in ångströms and orbital energies are in hartrees. Mulliken populations are for one of the equivalent centers. [b] This orbital energy becomes unrealistic for large values of R_{CH}, as a two-configuration description of the electronic structure becomes mandatory. Such a two-configuration SCF wave function at R_{CH} = 6.0 yields a $7a_g$ orbital energy of −0.4987 hartree. The Mulliken populations are not significantly changed in this TCSCF wave function.

Swenson and Hoffmann quite strictly, we should not expect an n_a-n_b reversal in CO-CO.

The representation in Figure 6 may explain this order reversal and the details of the through-bond interaction. The orbitals in which the hydrogens are most important are the $7a_g$, $6b_u$, $6a_g$, and $5a_g$. In the $7a_g$ (n_a) MO, delocalization of the n electrons on carbon is stabilized by the hydrogens. But the carbon 2p is out of phase with the oxygen 2p, making the C-O interaction destabilizing. Because the carbon AO's must combine antisymmetrically in the n_b ($6b_u$) MO, delocalization is inhibited and the Mulliken populations in Table VI show the $6b_u$ to be more localized on oxygen than the $7a_g$.

The $6a_g$ MO in *trans*-glyoxal is much like a C-O σ bond and the $5a_g$ like a C-C σ bond. When the hydrogens are withdrawn, the stability of the $5a_g$ would tend to be reduced (see Figure 6). As a result, the oxygen 2p AO's which form the $5a_g$ change to make it look more like the original $6a_g$. That is, while it still has C-C bonding character, it also has C-O bonding character (in CO-CO). The $6a_g$ now becomes the n_a orbital. Unlike the glyoxal n_a ($7a_g$), the interaction is almost exclusively through the carbon 2p orbitals perpendicular to the C-C axis. The form of the $6a_g$ orbital in CO-CO seems to be a result of the changed structure of the $5a_g$ orbital and is thus an indirect result of the removal of the hydrogens.

The $6b_u$ (n_b) orbital becomes increasingly carbon 2s like as the hydrogens are removed from glyoxal. But again, the 2s orbitals are out of phase and so, as seen in Figure 5, the $6b_u$ is destabilized in CO-CO. The $5b_u$ in CO-CO assumes some of the n character of the $6b_u$ and it might even be appropriate, though perhaps unconventional, to designate it as the n_b orbital. The change in orbital energy of the $5b_u$ upon removal of the hydrogens is about 0.04 hartree, which is about the same as the change in the $6a_g$, 0.06 hartree. But the $6b_u$ is raised by 0.12 hartree confirming the indirect effect of the hydrogens. We expect the orbital energies to be raised when the hydrogens are removed, but the $6a_g$ and $5b_u$ are not raised as much as the $6b_u$ because of reorganization of the orbital structures.

From these considerations (similar arguments may be made for *cis*-glyoxal), it seems clear that the extent of interaction in α-dicarbonyls is not small. And important in the interaction in say R-$(CO)_2$-R′ is the nature (or presence) of R and R′. In glyoxal, the presence of hydrogens makes delocalization of n electrons possible, depending on the phases of the contributing AO's. Without the hydrogens, not only is the n_a-n_b order reversed, but also the n_a and n_b orbitals are noticeably changed. Chemically, some generalizations are possible. For instance, substitution of an alkyl group for hydrogen, such as in biacetyl, should improve stability of the α-diketone. The interaction of the n_a orbital is expected to increase since delocalization of the electrons over the alkyl group would be greater than with hydrogen. We would expect the n_a stability to be improved relative to the n_b and therefore would expect a smaller n_a-n_b separation in biacetyl than glyoxal. It may also be possible to select R and R′ to sufficiently destabilize the valence orbitals to prevent the formation of a stable molecule. We hope to test this in a later study.

An important consequence of the ordering of the n and π valence MO's in glyoxal is the nature of the low-lying excited states. As can be seen from Figure 4, the lowest excited states are probably excitations from the n_a orbital. However, in contrast to all but the semi-empirical calculations of Kato et al.,[35] excitations from the highest π MO should also yield low-lying electronic states. This is a direct result of the n and π MO's not being completely energetically separate as often believed. In a preliminary calculation on the excited states of glyoxal, we have, in fact, found that $\pi \rightarrow \pi^*$ excited states are among the $n \rightarrow \pi^*$ states.

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References and Notes

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