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On the Origin of Transannular Interactions in Diketones and Methylene–Ketones, as Detected by ^{13}C N.M.R. Spectroscopy: An *ab initio* MO Study

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Abstract: Possible causes of the observed shifts of the ^{13}C n.m.r. resonances in diketones and methylene–ketones have been investigated by carrying out Weinhold natural population analyses (at the HF/6–31G(d) level) on a series of diketones, **6a** – **13a**, methylene–ketones, **17a** – **21a**, and the corresponding monofunctional reference molecules. The results show marked changes in electron density about the unsaturated groups in the difunctionalized molecules, relative to the monofunctional systems, and that these changes generally parallel the observed changes in the n.m.r. chemical shifts in these molecules. Calculations on model systems suggest that both the electron density shifts and the observed n.m.r. shift values in diketones and methylene–ketones are due to simple dipole–dipole electrostatic effects.

INTRODUCTION

A number of papers has appeared presenting interesting observations of patterns of changes in ^{13}C n.m.r. chemical shift values of sp^2 carbon nuclei in the difunctional systems, diketones, **1**, methylene–ketones, **2**, and bismethylenes, **3**, relative to their respective monofunctional congeners, **4** and **5**.[1–6] The following generalizations were made concerning the direction of change in the chemical shift of the sp^2 carbon nucleus in these molecules: The carbonyl carbon resonance in diketones, **1**, and in mixed methylene–ketones, **2**, appeared upfield, relative to the carbonyl resonance in the reference ketone, **4**. The quaternary and secondary carbon resonances in the mixed systems, **2**, and in the bismethylenes compounds, **3**, appeared, respectively upfield and downfield, with respect to the appropriate reference methylene compound, **5**.

1 X,Y = O
2 X = O; Y = CH_2
3 X,Y = CH_2

4 X = O
5 X = CH_2

The relative shielding of the carbonyl carbon nuclei in diketones is clearly seen in the representative series of mainly rigid molecules, **6** – **12**, the data for which are presented in Table 1. The Δδ values in this Table are equal to the chemical shift (in ppm) of the carbonyl carbon in the diketone minus the chemical shift of the carbonyl carbon in the monoketone (both measured in $CDCl_3$). A negative value for Δδ means an upfield shift of the carbonyl carbon resonance in the diketone, relative to the monoketone. The molecules in Table 1 are listed in the order of increasing separation between the carbonyl carbon atoms (the distances listed in this Table were obtained from HF/3-21G optimized structures; *vide infra*). Two important conclusions may be drawn from these data. Firstly, Δδ is negative for all compounds listed and this has been found to hold true for a wide range of diketones.[3–5] Secondly, the absolute magnitude of Δδ decreases with increasing intercarbonyl separation.

Clearly, the sizeable Δδ values observed for the diketones are caused by some kind of transannular interaction occurring between the carbonyl groups which presumably results in an increase in the electron density surrounding the carbonyl carbon nuclei, compared to the respective monoketones.[3–5] Two basic types of transannular interactions have been proposed to account for the n.m.r. results, namely, Hoffmann-type orbital interactions[7] and electrostatic interactions. The former may be subdivided into orbital interactions through-space (OITS) and orbital interactions through-bonds (OITB), depending on whether the interactions between the orbitals of the carbonyl groups occur through their direct, through-space (TS) overlap, or whether they occur by way of their mutual overlap with the orbitals of the intervening saturated molecular framework.[7–10]

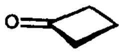
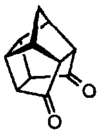
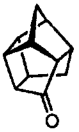
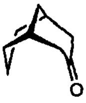
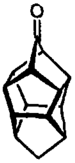
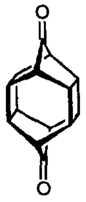
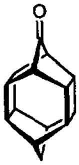
Reorganization of electron density in the carbonyl groups of diketones might also be realized by electrostatic dipole–dipole interactions between the carbonyl groups. This mechanism is explained in more detail below. Both types of mechanisms, orbital interactions and electrostatic interactions, have also been invoked to explain the Δδ values deduced from the ^{13}C n.m.r. spectra of methylene–ketones, **2**, although the magnitudes of the shifts in the C=C and C=O resonances for these compounds are generally not as large as those observed for the diketones.[3,5]

No clear consensus has yet been reached as to which mechanism, orbital interactions or electrostatic effects, is mainly responsible for the observed n.m.r. shifts in diketones and methylene–ketones. This problem has now been addressed using *ab initio* MO theory.[11] This approach should provide useful insight into the present problem since *ab initio* MO theory[11] enables one to calculate electron density distributions and to dissect, semiquantitatively, interactions into various components.[12]

This paper presents the results of calculations of the electron density distribution in the series of diketones, **6a** – **13a**, and the respective monoketone reference systems, **6b** – **13b**. These molecules were chosen because (with the exception of **13a** and **13b**) they represent a broad cross section of diketones that have been studied experimentally, in terms of both intercarbonyl separation (ranging from 2.1 Å to 5.1 Å) and intercarbonyl orientation. The, as yet unknown garudane[13] ketones, **13a** and **13b**, were included in this study in order to compare electron density reorganization in **13a** with that in **12a**. Although the intercarbonyl separations in **12a** and **13a** are similar, the carbonyl groups have different orientations with respect to each other in the two molecules. Consequently, orbital interactions between the carbonyl groups should have quite different magnitudes in **12a** and **13a**, whereas electrostatic interactions in these molecules should be of comparable strength. Thus, comparison of the results of calculations for **12a** with those for **13a** could provide useful insight into the relative importance of orbital interactions and electrostatic effects that are operating in these diketones.

Although the main thrust of the present work is to explore interactions in diketones, some calculations have also been carried out on the series of methylene–ketones, **17a** – **21a**, and the corresponding methylene reference systems, **17b** – **21b**. These results are also included and briefly discussed in this paper.

Table 1. ^{13}C n.m.r. Chemical Shift Differences, Δδ, for Carbonyl Carbon in Diketones

Molecules				R (Å)[a]	Δδ[b]
6a		**6b**		2.124	−10.7[c]
7a		**7b**		2.574	-9.5[d]
8a		**8b**		2.856	-5.8[d]
9a		**9b**		2.912	-3.7[c]
10a		**10b**		2.921	-3.9[d]
11a		**11b**		3.463	-4.9[d]
12a		**12b**		5.265	-3.8[e]
13a		**13b**		5.147	—

[a] Distance between the carbonyl carbon atoms of the carbonyl groups in the diketones, **6a – 13a**.

[b] Chemical shift (ppm) of carbonyl C nucleus in diketone minus that in monoketone (CDCl$_3$ solvent).

[c] Data from Ref. 4c.

[d] Data from Ref. 3b.

[e] Data from Ref. 5.

COMPUTATIONAL DETAILS

All calculations were carried out using the GAUSSIAN 92 suite of programs.[14] Full geometry optimizations of diketones and monoketones, **6–13**, and the methylene–ketones and methylene systems, **17- 21**, were carried out at the restricted Hartree–Fock (HF) level using the Schlegel analytical gradient procedure[15] and the split–valence 3–21G basis set (*e.g.*, HF/3-21G).[16] Geometry optimizations were carried out under the following symmetry constraints: D_{2d} symmetry for **11a** and **12a**; D_{2h} symmetry for **13a**; C_{2v} symmetry for **6a, 10a, 11b, 12b, 13b, 20a, 20b, 21a,** and **21b**; C_{2h} symmetry for **9a**; C_2 symmetry for **8a**; C_s symmetry for **6b, 7a, 9b, 10b, 19a,** and **19b**; C_1 symmetry for **7b, 8b, 17a, 17b, 18a,** and **18b**. Harmonic vibrational frequency calculations were carried out on **10a, 10b, 19a,** and **19b**, using analytically calculated first and second energy derivatives, in order to verify that the optimized structures actually correspond to genuine energy minima, which are confirmed by the presence of all real frequencies. Single point HF calculations were then carried out on the HF/3–21G optimized geometries using the 6–31G(d) basis set[16] which adds a set of six Cartesian *d*–type polarization functions to each nonhydrogen atom (*e.g.*, HF/6–31G(d)//3–21G). Natural population analyses (NPA) were carried out at this level of theory using the method of Weinhold *et al.*,[17] as implemented in GAUSSIAN 92. The effect of electron correlation on electron density distributions in **6a** and **6b** was carried out at the second–order Møller–Plesset level of theory[18] using the 6–31G(d,p) basis set which differs from the 6–31G(d) basis set in the addition of an extra set of three *p*–type polarization functions on each hydrogen atom.

RESULTS AND DISCUSSION

Molecular geometries

As mentioned above, molecular geometries for all systems studied were fully optimized under appropriate symmetry constraints at the Hartree–Fock (HF) level of theory, using the 3–21G basis set. This theoretical model is known to give reliable geometries for a wide range of polycyclic systems.[11,19] The structures of the bicyclo[3.3.1]nonane systems, **10a, 10b, 19a,** and **19b**, were optimized assuming that their lowest energy conformations are of the double chair type (which is reasonable[3]) and that they possess strict C_s symmetry (C_{2v} symmetry, in the case of **10a**). The validity of the symmetry constraints that were imposed on these geometry optimizations was checked by carrying out harmonic vibrational frequency calculations. In each case the calculated frequencies were all found to be real, thereby confirming that the optimized geometries for **10a, 10b, 19a,** and **19b** do, in fact, correspond to genuine energy minima.

Problems associated with calculating atomic charges in molecules

A major aim of this paper is to determine whether there is any substance to the notion that the observed negative $\Delta\delta$ values for diketones is attributed to migration of electron density towards the carbonyl carbon atom, relative to the reference monoketone. In principle, *ab initio* MO theory should be able to answer this question by simply calculating the charge on the carbonyl carbon atom in the diketone and reference monoketone and subtracting the latter result from the former. However, the situation is not so clear–cut as this recipe would imply. This is because allocation of electron density to atoms in molecules is a purely arbitrary process; atomic charge is not an observable and consequently, any definition of atomic charge must be arbitrary. This issue has been discussed at length in a recent excellent review[20] and herein only a brief survey of methods for calculating atomic charges in molecules will be presented.

In spite of this ambiguity associated with calculating atomic charges, several useful methods have been devised for calculating atomic charges, the "goodness" of any method being judged in terms of whether it is able to provide results that are chemically reasonable and which are noncontradictory for a wide range of molecules. Two major methods in use are the orbital–based method and the topological method. The former method assigns electrons to atoms in molecules based on the occupancy of the atomic orbitals which are generally centred on the nuclei. Within this method fall the Mulliken population analysis (MPA)[21] and the natural population analysis (NPA) of Weinhold *et al.*[17] The topological method[22] subdivides physical space into volumes (atomic basins) that are associated with specific atoms. Thus, the electron density associated with a particular atom in a molecule is found by integrating the electron density throughout that atom's atomic basin.

Both methods have their strengths and weaknesses,[20] although the topological method is quantum mechanically more rigorous than orbital–based methods. Nevertheless, in this work, the orbital–based Weinhold NPA method was used to calculate atomic charges. Of all the orbital–based approaches, the NPA method recognizes and attempts to define the spatial extent of an atom in a molecule.[20] In addition, the NPA method avoids the disastrous consequences that plague the MPA method, such as extreme sensitivity to the choice of basis set and unphysical orbital electron densities.[20]

Effects of basis set and electron correlation

Although it would be desirable to calculate atomic charges using a very large basis set of near Hartree–Fock quality, together with the inclusion of electron correlation, the size of the systems studied have restricted the choice to the Hartree-Fock level (*i.e.*, no electron correlation) of theory and the 6–31G(d) basis set. However, this basis set should be sufficiently flexible to provide reliable atomic charges and there is evidence that this is indeed, the case.[20] Nevertheless, prudence dictates that the effect of basis set and electron correlation should be carried out, at least on the smallest systems studied, namely, **6a** and **6b** and the results are presented in Table 2.

In this Table are presented Weinhold NPA atomic charges (in units of electronic charge, *e*) for the C and O atoms of the carbonyl group, together with the charge differences, Δ(C) and Δ(O) (in m*e* = 10^{-3} *e*). Throughout this paper, the latter quantities are defined as the atomic charge (in m*e*) of an atom in the diketone (or methylene–ketone) minus the atomic charge of the same atom in the appropriate reference molecule. Thus, a negative (positive) sign for Δ(X) implies a gain (loss) of electrons associated with atom X in the diketone (or methylene–ketone), compared to the reference molecule.

Table 2. Carbonyl C and O Atomic Charges for **6a** and **6b**, and Charge Differences, Δ(C) and Δ(O), Calculated Using the Weinhold NPA Method

		Atomic charges (*e*)[a]			
Molecule	Atom	HF/6–31G(d)	HF/6–31G(d,p)	HF/6–311+G(d,p)	MP2/6–31G(d,p)
6a	C	0.6893	0.6907	0.6819	0.5845
	O	–0.5943	–0.5948	–0.5979	–0.4698
6b	C	0.7035	0.7046	0.6972	0.5903
	O	–0.6174	–0.6175	–0.6248	–0.4855
		Atomic charge differences (x10^3 *e*)			
	Δ(C)[b]	–14.2	–13.9	–15.3	–5.8
	Δ(O)[b]	23.1	22.7	26.9	15.7

[a] Atomic charges are given in atomic units (charge of electron = –1 in these units).

[b] Atomic charge in **6a** minus atomic charge in **6b**, given in millielectrons (m*e*).

Three different basis sets were explored at the Hartree–Fock level which, in the order of increasing flexibility are: 6–31G(d), 6–31G(d,p), and 6–311+G(d,p). The first two basis sets are of double split-valence quality, augmented with a set of *d*–type polarization functions for each nonhydrogen atom and, in the case of the 6–31G(d,p) set, with an additional set of *p*–type polarization functions on each hydrogen atom. The 6–311+G(d,p) basis is of triple split-valence quality which includes polarization functions on all atoms together with a set of *s*– and *p*–type diffuse functions for every nonhydrogen atom.[11]

The data of Table 2 clearly show that the results are largely basis set independent: The atomic charges differ by only 3 – 7 m*e*, between the 6–31G(d) and 6–311G+(d,p) basis sets, while the Δ(C) and Δ(O) values differ by less than 4 m*e*. Such is not the case for the corresponding Mulliken charges (not shown) which differ by more than 250 m*e* between these two basis sets. The effect of electron correlation was examined at the MP2 level using the 6–31G(d,p) basis set. The absolute values of the atomic charges decrease by 105 – 131 m*e* upon inclusion of electron correlation, and this is not surprising since electron correlation is known to cause a substantial reduction of charge separation, particularly in unsaturated bonds, relative to the Hartree–Fock level of theory.[11,20] The Δ(C) and Δ(O) values are, respectively, about 2.4 and 1.4 times smaller at the correlated level, than at the Hartree–Fock level. Importantly, the signs of Δ(X) remain the same at both levels of theory, being negative for Δ(C) and positive for Δ(O).

In summary, HF/6–31G(d) theory should give qualitatively acceptable results, although quantitative treatments would require population analyses to be carried out on electron–correlated wavefunctions.

Atomic charge differences for diketones, **6a** – **13a**.

The relevant data for **6a** – **13a** are given in Table 3. For the sake of brevity, the atomic charges for the carbonyl C and O atoms are not presented, and only the charge differences, Δ(X) (X = C, O), which are the important quantities, are listed.

Table 3. Chemical Shift Differences, Δδ, for the Carbonyl Carbon Atom, and HF/6–31G(d) Atomic Charge Differences, Δ(C) and Δ(O), for the Carbonyl Carbon and Oxygen Atoms in **6a** – **13a**

Diketone	R (Å)[a]	Δδ (ppm)[b]	Δ(C)[c] (NPA)	Δ(O)[d] (NPA)	Δ(C)[e] (MPA)
6a	2.124	-10.7[f]	-14.2	23.1	2.2
7a	2.574	-9.5[g]	-15.0	26.8	-11.0
8a	2.856	-5.8[g]	-7.5	15.5	2.4
9a	2.912	-3.7[f]	-8.5	15.4	-3.4
10a	2.921	-3.9[g]	-17.3	32.5	-21.0
11a	3.463	-4.9[g]	-4.5	9.9	5.5
12a	5.265	-3.8[h]	-0.6	7.2	0.4
13a	5.147	—	-2.4	8.1	-0.4

[a] Distance between the carbon atoms of the carbonyl groups in the diketones, **6a** – **13a**.

[b] Chemical shift of carbonyl C nucleus in diketone minus that of carbonyl C nucleus in monoketone.

[c] NPA Atomic charge (in m*e*) on C in diketone minus atomic charge on C in monoketone.

[d] NPA Atomic charge (in m*e*) on O in diketone minus atomic charge on O in monoketone.

[e] Mulliken (MPA) Atomic charge on C in diketone minus atomic charge on C in monoketone, in m*e*.

[f] Data from Ref. 4c.

[g] Data from Ref. 3b.

[h] Data from Ref. 5.

The $\Delta(C)$ values for all members of the series of diketones, **6a** – **13a**, are negative quantities, whereas the corresponding $\Delta(O)$ values are all positive. Thus, relative to the monoketones, electron density associated with the carbonyl carbon atom is increased in **6a** – **13a**, but is depleted about the oxygen atom. This is not the case for the $\Delta(C)$ values, calculated using the Mulliken (MPA) method (last column of Table 3), which are negative for four diketones but positive for the remaining four. This erratic behaviour underscores the unreliability of the MPA method.

The NPA calculations support the idea that the upfield chemical shifts of the carbonyl carbon resonances in diketones (*i.e.*, negative $\Delta\delta$ quantities) result from increased electron density about these nuclei, compared to the respective monoketone reference molecules.[3–5] Moreover, the absolute magnitude of the $\Delta(C)$ values for the series **6a** – **13a** generally decreases with increasing intercarbonyl separation, in agreement with the behaviour of the corresponding n.m.r. $\Delta\delta$ values. However, **10a** is an exception to this trend, since $\Delta(C)$ for this system is calculated to be the most negative for all systems studied. Moreover, whereas $\Delta(C)$ for **10a** is *more* negative than its neighbours, the corresponding $\Delta\delta$ value is *less* negative. The reason for this anomaly is unknown, although conformational effects, such as the possible existence of boat conformations in **10a** and/or **10b** seem to be an unlikely cause.[23]

The NPA results for **6a** – **13a** indicate that, although electron density reorganization occurs within the carbonyl groups in diketone systems, compared to the monoketone reference, the total density is not conserved, in that the oxygen atom loses about twice as much electron density as that gained by the carbon atom. Therefore, compared to the respective monoketone reference molecules, electron density "leaks" from the carbonyl groups in **6a** – **13a** into the surrounding saturated hydrocarbon framework.

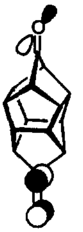
Origin of electron density reorganization in diketones, **6a** – **13a**.

It seems reasonable to assume that both observed upfield shifts in the carbonyl ^{13}C resonances and the corresponding shifts in the calculated electron density about the carbonyl group in **6a** – **13a** have a common origin. The question is what type of transannular interaction between the carbonyl groups in the diketone systems is responsible for these effects, orbital interactions or electrostatic, or both?

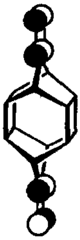
The OITS/OITB mechanisms are appealing because a large body of experimental evidence, based largely on photoelectron (PE) spectroscopic studies, has convincingly demonstrated the existence of such interactions in a wide variety of diketones.[9] However, it is not clear whether the types of orbital interactions that are measured by PE spectroscopy could be the cause of the observed n.m.r. chemical shift data and calculated electron density reorganizations for the carbonyl groups. This is because the type of orbital interaction needed to achieve the required electron density reorganization must involve the (through–space or through–bond) mixing of a filled orbital (C=O π MO or the energetically higher lying oxygen *p*–type lone pair orbital, n_p) of one carbonyl group with the vacant π^* orbital of the other carbonyl group, and *vice versa*. However, the large magnitudes of the TS and TB orbital interactions observed in the PE spectra of diketones arise predominantly, if not exclusively, from interactions between the filled n_p orbitals of the two oxygen atoms. Consequently, the PE spectroscopic data do not provide direct information concerning the existence and extent of orbital interactions between filled and vacant orbitals of the carbonyl groups in diketones and, for this reason, it is probably not legitimate to cite the PE spectroscopic data as evidence for the existence of the type of orbital interactions that might cause electron density reorganization in diketones.

The sizeable magnitudes of $\Delta\delta$ for adamantane–2,6–dione, **11a** (and the related noradamantane-2,6-dione)[3] and for the heptacyclic diketone, **12a**,[5] have led some investigators to question whether orbital interactions play any role at all in affecting the carbonyl chemical shifts,[2a,3,5] on the grounds that OITS and OITB in these diones are rigorously excluded for symmetry reasons. Because these diones possess D_{2d} symmetry, mixing between the following pairs of orbitals located on different carbonyl groups, $\{n_p,n_p\}$, $\{\pi,\pi\}$, and $\{\pi^*,\pi^*\}$[24] is strictly forbidden, no matter whether the attempted mixing occurs through–space or through–bonds. Indeed, the PE spectra of such D_{2d} diketones reveal no $\{n_p,n_p\}$ splittings and MO calculations show that the n_p, π and π^* levels in these systems are each doubly degenerate.[10] However, for reasons given above, such interactions are probably unimportant to the matter in hand and one should focus attention instead, on interactions between filled and vacant orbitals, *i.e.*, $\{\pi,\pi^*\}$ and $\{n_p,\pi^*\}$. Although $\{\pi,\pi^*\}$ interactions are forbidden in **11a** and **12a**, $\{n_p,\pi^*\}$ interactions are not, as can be seen from inspection of **14a**. Indeed, *ab initio* MO calculations on **12a**, using localized orbitals, indicate that $\{n_p,\pi^*\}$ interactions are present in this molecule, although they are weak.[10] The reverse situation is found to obtain for diketones possessing D_{2h} symmetry, such as **13a**, in that $\{\pi,\pi^*\}$ and $\{n_p,\pi^*\}$ interactions are, respectively, allowed and forbidden, as shown by **14b**.

14a $\{n_p,\pi^*\}$ (and $\{n_p,\pi\}$) interactions are allowed; $\{\pi,\pi^*\}$ and $\{\pi,\pi\}$ interactions are forbidden

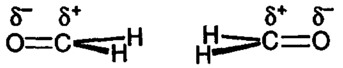


14b $\{\pi,\pi^*\}$ (and $\{\pi,\pi\}$) interactions are allowed; $\{n_p,\pi^*\}$ and $\{n_p,\pi\}$ interactions are forbidden

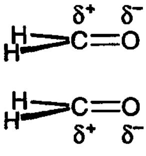


In summary, in spite of previously expressed concerns,[2a,3,5] symmetry arguments alone cannot exclude orbital interactions from playing a major role in modulating electron density distribution within the carbonyl groups in D_{2d} diketones, such as **11a** and **12a**. It is, therefore feasible that OITS and/or OITB could be responsible for the observed trends in the $\Delta\delta$ values for *all* diketones studied, including **11a** and **12a**. Of the two types of orbital interactions, OITB is a more likely candidate than OITS because through-space interactions decay much more rapidly with increasing interorbital separation than do OITB, and become negligible at separations beyond 5 Å.[8a,8d] Such a strong distance dependence is not reflected by the $\Delta\delta$, Δ(C), and Δ(O) values for **6a** – **13a** (Table 3) which are significant even for **12a** and **13a** for which the intercarbonyl separation is greater than 5 Å. In addition, although the intercarbonyl separation in **12a** is more than double that in **6a**, the magnitude of $\Delta\delta$ in the former diketone is only 2.8 times smaller than that found for the latter. The fairly weak distance dependence of the magnitudes of $\Delta\delta$ and Δ(X) (X = C, O) is more in keeping with the operation of a TB mechanism, rather than a TS mechanism, since it has been demonstrated experimentally that TB interactions display only a weak exponential distance dependence.[7,8]

Electrostatic effects have also been invoked to explain the $\Delta\delta$ values, partly in reponse to the (spurious) symmetry arguments that were applied to diketones **11a** and **12a**. The electrostatic argument can be appreciated from consideration of **15a** and **15b** which depict two different orientations of a pair of formaldehyde molecules. In orientation **15a**, the carbonyl dipoles are pointing in opposite directions; consequently, the positive end (*i.e.*, carbon) of the dipole of one of the carbonyl groups induces electron density migration to occur in the other carbonyl group, from oxygen (*i.e.*, the negative end) to carbon, and *vice versa*. The degree of electron density reorganization resulting from this dipole – dipole interaction naturally depends on both the distance between the dipoles and on their orientation with respect to each other. For example, electron density reorganization within the carbonyl groups should be greater in the parallel orientation, **15b**, than in the antiparallel orientation, **15a**, on account of a combined push – pull effect operating in the former orientation, resulting from the "pushing" of electron density towards the carbon atoms of both carbonyl groups by electrostatic interactions between the pair of proximate (negative) oxygen atoms, and the reinforcing "pulling" of electron density, in the same direction, by electrostatic interactions between the (positive) carbon atoms.



15a

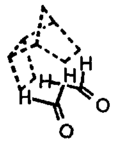


15b

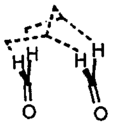
Within the context of the current series of diketones, it is noted that the orientation of the carbonyl groups in **6a**, **11a–13a**, and to a lesser extent, in **8a**, is similar to that depicted by **15a**. In contrast, the intercarbonyl orientation in **7a** and **10a** resembles **15b**, although the angle between the planes of the two carbonyl groups in these molecules is 67° and 32°, respectively (the corresponding interplanar angle in **15b** is, of course, 0°). This may explain why the electron density reorganization, as measured by the Δ(C) values (Table 3) is larger for **7a** and **10a**, compared to that for **6a** and **8a**, even though the intercarbonyl separation in **7a** is greater than in **6a**, as is also the case for **10a**, compared to **8a**.

Experimental evidence for an electrostatic cause of the observed Δδ values for the diketones is scant and mainly rests on the observation that the magnitude of Δδ for **12a** is reduced from a value of –3.8 ppm, in $CDCl_3$ solvent, to only –0.9 ppm in CD_3OD solvent. Electrostatic dipole – dipole interactions between the carbonyl groups in **12a** are expected to be much weaker in CD_3OD, owing to the greater polarity and stronger hydrogen bonding ability of CD_3OD, compared to $CDCl_3$.[5]

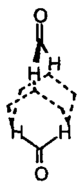
Finally, through–space electrostatic dipole–dipole interactions display a weak distance dependence, varying inversely with the cube of the interdipole separation and this is not inconsistent with the weak distance dependence shown by the Δδ, Δ(C), and Δ(O) values found for the series of diketones **6a – 13a**.



7aM

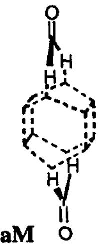


10aM



11aM

12aM



13aM

Model calculations using bisformaldehyde complexes

Two likely candidates for explaining the observed ^{13}C n.m.r. chemical shift data and the calculated electron density shifts, Δ(X) in the diketones, **6a – 13a**, emerge from the preceding discussion, namely OITB and (through–space) electrostatic dipole – dipole interactions. Although it is not possible to dissect *directly*, the calculated Δ(X) data for the "real" systems, **6a – 13a**, into OITB and electrostatic contributions, an indirect estimate of the relative importance of OITB and electrostatic effects in these systems may be obtained by carrying out calculations on a series of model complexes, comprising two formaldehyde molecules whose separation and orientation with respect to each other mimic the disposition of the two carbonyl groups in the diketone series, **6a – 13a**. Bisformaldehyde models for **7a** and **10a – 13a** are designated by **7aM** and **10aM – 13aM**, respectively. Because through–bond interactions between the carbonyl groups are absent in these complexes, comparison of electron density reorganization in these complexes with that in the corresponding "real" diketones, **7a** and **10a – 13a**, should provide an estimate of the relative importance of the OITB contribution towards electron density reorganization in the latter series.

Model complexes for **6a**, **8a**, and **9a** were not examined on the grounds that the closeness of the hydrogen atoms belonging to different formaldehyde molecules (< 2 Å) in these complexes introduces unwanted TS interactions between the formaldehyde molecules (*via* H---H orbital overlap) that are obviously absent in the parent systems, **6a**, **8a**, and **9a**. For similar reasons, the seemingly more appropriate models for **7a** and **10a** – **13a**, comprising two acetone molecules were not considered, since unwanted through–space interactions between the bulky methyl groups would be present in these complexes.

The results for the model bisformaldehyde complexes are presented in Table 4. The Δ(X) (X = C, O) values for the complexes were calculated relative to the corresponding NPA atomic charges for an isolated formaldehyde molecule. The data immediately reveal a qualitative correspondence between the Δ(X) values for the series of diketones and their respective model complexes. Compared to the respective parent diketones, **7a** and **10a** – **13a**, the absolute values of Δ(C) for the complexes are slightly larger, whereas, with the exception of **11a**, the Δ(O) values for the complexes are slightly smaller. The Δ(X) values for **12aM** and **13aM** are nearly equal to each other, which is to be expected for a purely electrostatic effect operating between two carbonyl groups separated by essentially the same distance. Rotation of one of the carbonyl groups by 90° about the C=O axis in **11aM** and **13aM** had no effect on the Δ(X) values in these molecules (Table 4, data in parentheses), thereby confirming again the importance of pure electrostatic effects operating in these complexes.

Table 4. HF/6–31G(d) Atomic Charge Differences, Δ(C) and Δ(O), for the Carbonyl C and O Atoms of **7a**, **10a** – **13a**, and the Model Bisformaldehyde Complexes, **7aM**, **10aM** – **13aM**

System	R (Å)[a]	Δ(C)[b]	Δ(O)[c]
7a	2.574	–15.0	26.8
7aM		–32.0	22.8
10a	2.921	–17.3	32.5
10aM		–22.5	20.5
11a	3.463	–4.5	9.9
11aM		–5.2 (3.3[d])	13.7 (13.4[d])
12a	5.265	–0.6	7.2
12aM		–3.1	6.0
13a	5.147	–2.4	8.1
13aM		–3.1 (–3.3[d])	6.4 (6.4[d])

[a] Distance between the carbon atoms of the carbonyl groups in the diketones, **7a, 10a – 13a.**

[b] NPA Atomic charge (m*e*) on C in diketone (or bisformaldehyde complex) minus that on C in monoketone (or formaldehyde).

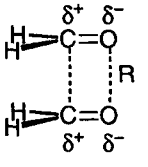
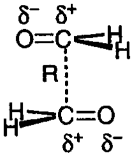
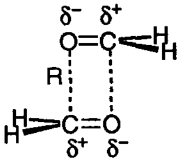
[c] NPA Atomic charge (m*e*) on O in diketone (or bisformaldehyde complex) minus that on O in monoketone (or formaldehyde).

[d] Δ(C) and Δ(O) values resulting from rotation of one formaldehyde molecule 90° about its carbonyl axis.

The good correspondence between the Δ(X) values for the diketones and their bisformaldehyde models convincingly suggests that electrostatic dipole – dipole interactions, and not OITB, are the main cause of the calculated electron density shifts in **7a–13a**, and that they are probably also responsible for the observed n.m.r. Δδ shifts in the same systems. It could be argued that OITS, in addition to electrostatic effects, could influence electron density reorganization about the carbonyl groups in **7a** on the grounds that the carbonyl groups in this molecule are only 2.6 Å apart (in contrast to the ≥ 3 Å separation found in the higher members of the series). Indeed, at the HF/6–31G(d) level, the n_p orbitals in **7a** are split by 0.75 eV, with the a' (in–phase) combination of n_p orbitals (*i.e.*, $n_p + n_p$) lying energetically below the a" (out–of–phase) combination (*i.e.*, $n_p - n_p$), which is symptomatic of net through–space interactions operating between these orbitals. However, as stressed above, $\{n_p,n_p\}$ interactions are not necessarily responsible for causing electron density shifts within the carbonyl groups.

That OITS are probably not influential in **7a** was deduced by carrying out calculations on the model complexes, **16**, the results of which are presented in Table 5. In these models, the formaldehyde molecules lie in parallel planes with respect to each other, at three different intercarbonyl distances, R. The CCO angles in each complex are held at 90°. The C_{2v} head–to–head complex, **16a**, with R = 2.5 Å, is an idealization of the disposition of the carbonyl groups found in **7a**. The corresponding C_{2h} head–to–tail complex, **16c**, differs from **16a** in that the C=O dipoles are aligned in an antiparallel manner.

Table 5. HF/6–31G(d) Atomic Charge Differences, Δ(C) and Δ(O), for the Carbonyl C and O Atoms in Model Bisformaldehyde Complexes

R (Å)	Δ(X)[a]	 **16a**	 **16b**	 **16c**
2.92	Δ(C)	-25.0	-3.0	28.2
	Δ(O)	25.0	-16.9	-38.9
2.5	Δ(C)	-42.3	-12.7	50.2
	Δ(O)	32.2	-26.5	-70.8
2.0	Δ(C)	-84.6	-48.9	127.6
	Δ(O)	37.4	-41.6	-178.0

[a] NPA atomic charge on C or O in bisformaldehyde complex minus respective atomic charge in formaldehyde molecule.

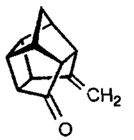
HF/6–31G(d) calculations on these bisformaldehyde models reveal that $\{\pi,\pi\}$, $\{\pi^*,\pi^*\}$, and $\{n_p,n_p\}$ through–space orbital interactions are of comparable magnitude for both **16a** and **16c**. For example, for an intercarbonyl separation of R = 2.5 Å, the calculated splittings for **16a** and **16c** (in parentheses) are: 2.7 (2.6) eV for $\{\pi,\pi\}$, 0.54 (0.44) eV for $\{\pi^*,\pi^*\}$, and 3.1 (2.5) eV for $\{n_p,n_p\}$. Consequently, if OITS played a major role in electron density reorganization in diketones, then Δ(X) should be of comparable magnitude in both **16a** and **16c**. The data in Table 5 clearly show that this is not the case, since the signs of Δ(C) and Δ(O) for **16a** are the opposite of the respective quantities in **16c**, for all three values of intercarbonyl separation. These results, although incompatible with an OITS mechanism, can be readily explained in terms of electrostatic effects. The alignment of dipoles in **16a** is well set up for promoting electron density migration from oxygen to carbon by the "push–pull" effect (*vide supra*). In contrast, for **16c**, the dipoles are oriented such that their mutual interaction results in movement of electron density in the opposite direction, *i.e.*, from carbon to oxygen, in each formaldehyde molecule. That is, each oxygen atom polarizes (repels) electron density in the neighbouring formaldehyde molecule, in the direction from carbon to oxygen, and each carbon atom polarizes (attracts) electron density in the neighbouring formaldehyde molecule, in the same direction, that is, from carbon to oxygen. This has the effect of making Δ(C) positive and Δ(O) negative, and this is precisely what is observed. As to be expected, the magnitude of this effect is found to increase with decreasing values of intercarbonyl separation, R.

Complex **16b** represents an intermediate situation between the two extreme orientations, **16a** and **16c**. Thus, for all values of intercarbonyl separation, R, studied, Δ(C) for **16b** is negative, but its absolute magnitude is smaller than that for **16a** because the oxygen---oxygen electrostatic interactions that "push" electron density towards the carbon atoms (*vide supra*) are much weaker in **16b**, compared to those in **16a**. In contrast to the situation for **16a**, Δ(O) for **16b** is negative, and this was also found to be the case for **16c**. No doubt this is the consequence of the oxygen atoms in **16b** interacting, electrostatically, with the (positively charged) hydrogen atoms of the neighbouring formaldehyde molecule.

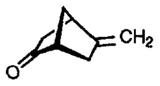
In summary, the calculated electron density shifts, Δ(C) and Δ(O), for **16a–16c** are consistent with the operation of an electrostatic mechanism, but not with an OITS based mechanism, even though large $\{\pi,\pi\}$, $\{\pi^*,\pi^*\}$, and $\{n_p,n_p\}$ TS interactions are calculated for these complexes (*vide supra*). Consequently, it would seem reasonable also to attribute an electrostatic cause of the calculated Δ(X) and observed $\Delta\delta$ n.m.r. shifts for **7a**, and possibly even for **6a**.

Electron density reorganization in methylene–ketones

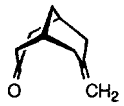
Weinhold natural population analyses were also carried out on the methylene–ketones, **17a** – **21a**, and on the methylene reference molecules, **17b** – **21b**, and the results are given in Table 6, together with the associated n.m.r. $\Delta\delta$ shifts.[3,5] Changes in the electron density and chemical shifts of the carbonyl group in **17a** – **21a** are calculated relative to the corresponding values in the respective monoketone molecules, **7b** – **12b**, and those associated with the methylene group are calculated relative to the corresponding values for the methylene group in the methylene molecules, **17b** – **21b**.



17a

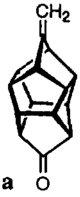


18a

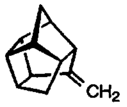


19a

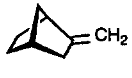
20a



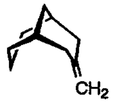
21a



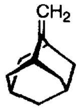
17b



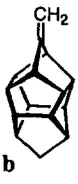
18b



19b



20b



21b

With the exception of **21a**, the following generalization may be made concerning the n.m.r. $\Delta\delta$ values for the methylene–ketones: The carbonyl carbon resonance is shifted upfield, and the methylene secondary and quaternary carbon resonances are shifted, respectively, downfield and upfield, all relative to the

Table 6. ^{13}C n.m.r. Chemical Shift Differences, Δδ, for Carbon Nuclei, and HF/6–31G(d) NPA Atomic Charge Differences, Δ(C) and Δ(O), in Methylene–ketones, **17a** – **21a**

methylene–ketone		*methylene* → *methylene–ketone*			*ketone* → *methylene–ketone*		
		$\Delta\delta^{a}$	$\Delta(C)^{b}$	$\Delta(O)^{c}$	$\Delta\delta^{a}$	$\Delta(C)^{b}$	$\Delta(O)^{c}$
17a	C=O	—	—	—	-4.1^{d}	2.9	8.3
	$>$C=	-5.1^{d}	−29.7	—	—	—	—
	=CH$_2$	2.4^{d}	34.2	—	—	—	—
18a	C=O	—	—	—	-1.5^{d}	−2.1	3.9
	$>$C=	-6.3^{d}	−15.6	—	—	—	—
	=CH$_2$	3.5^{d}	16.4	—	—	—	—
19a	C=O	—	—	—	-3.2^{d}	6.2	2.5
	$>$C=	-8.4^{d}	−40.6	—	—	—	—
	=CH$_2$	6.9^{d}	48.8	—	—	—	—
20a	C=O	—	—	—	-1.4^{d}	−0.9	2.2
	$>$C=	-4.8^{d}	−9.9	—	—	—	—
	=CH$_2$	2.9^{d}	10.6	—	—	—	—
21a	C=O	—	—	—	-1.1^{e}	−0.6	2.0
	$>$C=	0.7^{e}	−0.2	—	—	—	—
	=CH$_2$	1.7^{e}	5.9	—	—	—	—

[a] Chemical shift difference (ppm, CDCl$_3$ solvent) between specified C nucleus in methylene–ketone minus that in the appropriate reference molecule (*i.e.*, methylene system or monoketone).

[b] NPA Atomic charge (m*e*) on specified C atom in methylene–ketone minus that in appropriate reference.

[c] NPA Atomic charge (m*e*) on O atom in methylene–ketone minus that in monoketone reference.

[d] Data from Ref. 3b.

[e] Data from Ref. 5.

appropriate reference systems. The results for **21a** are consistent with this generalization with the exception that the methylene quaternary carbon experiences a small downfield shift, relative to that in **21b**.

The trends in the calculated atomic charge differences, Δ(C), for the methylene carbon atoms in **17a** - **21a** nicely parallel the corresponding trends in n.m.r. Δδ shifts, in that the secondary carbon atom loses electron density (*i.e.*, Δ(C) for this atom is positive) whereas the quaternary carbon gains electron density (*i.e.*, Δ(C) for this atom is negative), both relative to the respective atoms in the methylene reference systems. The only conflict between the signs of the Δ(C) and Δδ values occurs for the quaternary carbon atom in **21a**. However, in this case, the absolute magnitudes of Δδ and Δ(C) for this molecule are small and the discrepancy could well be due to neglect of solvent effects in the calculations and to inherent deficiencies in the theoretical model used.

The calculated Δ(C) values for the carbonyl group of **17a** – **21a** are less easily reconciled with the n.m.r. chemical shift data, since Δ(C) is negative only for **18a**, **20a**, and **21a**, whereas Δδ is negative for all five molecules.

The data for the methylene–ketones are best explained in terms of electrostatic interactions operating between the carbonyl and methylene groups. For all molecules studied, the carbonyl carbon atom is closer to the methylene quaternary carbon atom, than it is to the methylene secondary carbon atom. Consequently, the electrostatic influence of the carbonyl dipole should polarize the electron density in the methylene group, in the direction from the secondary carbon towards the quaternary carbon, and this is borne out by the calculations. The polarizing effect of the methylene group on the electron density distribution in the carbonyl group is less easily predicted because the bond dipole moment of the methylene group is expected to be small. For example, natural population analyses carried out on the methylene reference systems, **17b** – **21b**, all show that the atomic charges of the quaternary and secondary methylene carbon atoms are comparable in magnitude but that the quaternary carbon has a slight electron deficiency (of about 20 m*e*), compared to the secondary carbon atom. This finding would suggest that the methylene group in the methylene–ketones should induce a weak polarization of the electron density in the carbonyl group, towards the carbon atom. This is in agreement with the negative Δδ values observed for **17a** – **21a**, but is only partially consistent with the calculated signs for the corresponding Δ(C) values (although it is noteworthy that Δ(O) is found to be positive for all members of the methylene–ketone series).

CONCLUSION

Two major causes of the n.m.r. Δδ shifts in the ^{13}C n.m.r. carbonyl and methylene resonances in diketones and methylene–ketones have been advanced previously, namely, orbital interactions (through–space and/or through–bonds) and electrostatic dipole–dipole interactions. It is thought that such interactions should induce a reorganization of the electron density within the carbonyl and methylene groups.

This argument finds support from NPA–HF/6–31G(d) calculations on a series of representative diketones, **6a** – **13a**, and methylene–ketones, **17a** – **21a**. The results clearly show that electron density is greater around the carbonyl carbon atoms in all diketones studied, compared to the monoketone reference molecules. In addition, the variation in the magnitude of this electron density reorganization along the series **6a** – **13a**, is in general accordance with the corresponding changes in the ^{13}C n.m.r. Δδ values. Calculations on model bisformaldehyde complexes suggest that neither through–space nor through-bond orbital interactions plays an important role in the electron density reorganization process. Consequently, it is concluded that the calculated electron density reorganization in **6a** – **13a** is due simply to dipole–dipole electrostatic effects. It is also reasonable, therefore, to conclude that the same electrostatic effects are also responsible for the observed ^{13}C n.m.r. Δδ shifts in diketones.

The NPA results for the methylene–ketones **17a** – **21a** are also in accord with the operation of electrostatic effects causing both electron density and n.m.r. Δδ shifts for the methylene group in these molecules. However, the data for the carbonyl group in **17a** – **21a** are less conclusive.

Overall, it would appear that electrostatic effects adequately explain the observed ^{13}C n.m.r. $\Delta\delta$ data for diketones and methylene–ketones, and that orbital interactions probably play a only a minor role in these phenomena.

It is emphasized that the parallel behaviour found between the experimental ^{13}C n.m.r. $\Delta\delta$ shifts and the calculated $\Delta(C)$ values along the series **6a** – **13a** strongly suggests, *but does not demand*, that a nexus exists between the two quantities. Such a nexus might be placed on a more secure footing by carrying out n.m.r. chemical shift calculations on **6a** – **13a**, and particularly on a variety of model systems, such as **7aM**, **10aM** – **13aM**, and **16**, using *ab initio* methods such as IGLO,[25a] LORG,[25b] and GIAO.[25c] A correlation between the calculated n.m.r. shifts and $\Delta(C)$ values for the model systems would provide more convincing support for an electrostatic origin for the observed n.m.r. trends. This computationally demanding investigation is planned for the near future.

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REFERENCES AND NOTES

1. Senda, Y.; Ishiyama, J.; Imaizumi, S. *J. Chem. Soc., Perkin Trans. 2* **1981**, 90.
2. (a) Duddeck, H. *Tetrahedron* **1983**, *39*, 1365. (b) Majerski, Z.; Vinkovic, V.; Meic, Z. *Org. Magn. Reson.* **1981**, *17*, 169.
3. (a) Bishop, R. *Aust. J. Chem.* **1984**, *37*, 319. (b) Bishop, R.; Lee, G.–H. *Aust. J. Chem.* **1987**, *40*, 249.
4. (a) Doerner, T.; Gleiter, R,; Robbins, T. A.; Chayangkoon, P.; Lightner, D. A. *J. Am. Chem. Soc.* **1992**, *114*, 3235. (b) Robbins, T. A.; Toan, V. V.; Givens, J. W.; Lightner, D. A. *J. Am. Chem. Soc.* **1992**, *114*, 10799. (c) Gurst, J. E.; Schubert, E. M.; Boiadjiev, S. E.; Lightner, D. A., *Tetrahedron* **1993**, *49*, 9191.
5. Chow, T. J.; Wu, T.–K.; Shih, H.–J, *J. Chem. Soc., Chem. Commun.* **1989**, 490.
6. (a) Batchelor, J. G.; Prestergard, J. M.; Cushley, R. J.; Lipsky, S. R. *J. Am. Chem. Soc.*, **1973**, *95*, 6358. (b) Gunstone, F. D.; Pollard, M. R.; Scrimgeour, C. M.; Vedanayagam, H. S. *Chem. Phys. Lipids* **1977**, *18*, 115. (c) Bianchi, G.; Howarth, O. W.; Samuel, C. J.; Vlahov, G. *J. Chem. Soc., Chem. Commun.* **1994**, 627.
7. (a) Hoffmann, R. *Acc. Chem. Res.* **1971**, *4*, 1. (b) Hoffmann, R.; Imamura, A.; Hehre, W. J. *J. Am. Chem. Soc.* **1968**, *90*, 1499.
8. (a) Gleiter, R. *Angew. Chem. Int. Ed. Engl.* **1974**, *13*, 696. (b) Paddon–Row, M. N. *Acc. Chem. Res.* **1982**, *15*, 245. (c) Paddon–Row, M. N. *Acc. Chem. Res.* **1994**, *27*, 18. (d) Paddon-Row, M. N.; Jordan, K. D. in: *Modern Models of Bonding and Delocalization*; Liebman, J. F.; Greenberg, A., Eds.; VCH Publishers, NewYork, **1988**; 115.
9. Martin, H.–D.; Mayer, B. *Angew. Chem. Int. Ed. Engl.* **1983**, *22*, 283.
10. Albert, B.; Elsässer, D.; Martin, H.–D.; Mayer, B.; Chow, T. J.; Marchand, A. P.; Ren, C.–T.; Paddon–Row, M. N. *Chem. Ber.* **1991**, *124*, 2871.
11. Hehre, W. J.; Radom, L.; Schleyer, P.v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; John Wiley and Sons: New York, 1986.
12. (a) Heilbronner, E.; Schmelzer, A. *Helv. Chim. Acta* **1975**, *58*, 936. (b) Jordan, K. D.; Paddon–Row, M. N. *Chem. Rev.* **1992**, *92*, 395.

13. Mehta, G.; Padma, S. *J. Am. Chem. Soc.* **1987**, *109*, 7230.
14. Gaussian 92, Revision A, Frisch, M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, P. M. W.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; Martin, R. L.; Fox, D. J.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A., Gaussian, Inc., Pittsburgh PA, 1992.
15. Schlegel, H. B. *J. Comput. Chem.* **1982**, *3*, 214.
16. For a discussion of the 3–21G, 6–31G(d), 6–31G(d,p), and 6–311+G basis sets, as well as citations to the original literature, see Ref. 11.
17. (a) Reed, A. E.; Weinhold, F. *J. Chem. Phys.* **1983**, *78*, 4066. (b) Reed, A. E.; Weinstock, R. B.; Weinhold, F. *J. Chem. Phys.* **1985**, *83*, 735.
18. (a) Møller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618; (b) Pople, J. A.; Binkley, J. S.; Seeger, R. *Int. J. Quantum Chem., Symp.* **1976**, *10*, 1; (c) Krishnan, R.; Pople, J. A. *Int. J. Quantum Chem.* **1978**, *14*, 91; (d) Krishnan, R.; Frisch, M. J.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 4244.
19. (a) Castro, C. R.; Butler, R.; Rauk, A.; Wieser, H. *J. Mol. Struct. (Theochem)* **1987**, *152*, 241. (b) Paddon–Row, M. N.; Wong, S. S.; Jordan, K. D. *J. Am. Chem. Soc.* **1990**, *112*, 1710. (c) Paddon–Row, M. N.; Jordan, K. D. *J. Am. Chem. Soc.* **1993**, *115*, 2952.
20. Bachrach, S. M. *Reviews in Computaional Chemistry*, Lipkowitz, K. B.; Boyd, D. B., Eds., VCH, New York, 1994, Vol. V, 171.
21. Mulliken, R. S. *J. Chem. Phys.* **1955**, *23*, 1833.
22. Bader, R. F. W. *Atoms in Molecules – A Quantum Theory*, Oxford University Press, Oxford, 1990.
23. MM2 force–field calculations place the boat–chair conformations of **10a** and **10b**, respectively, 3.5 and 4.9 kcal/mol higher in energy than the double–chair structures, as depicted in Table 1. Consequently, the populations of the boat–chair conformations of these molecules are negligible at ambient temperature.
24. Note that the contents of each bracket represents two sets of interactions; *e.g.*, $\{\pi,\pi^*\}$ represents interaction of the π orbital of one carbonyl group with the π^* orbital of the other carbonyl group, and *vice versa.*
25. (a) Kutzelnigg, W. *Isr. J. Chem.* **1980**, *19*, 193. (b) Hansen, A. E.; Bouman, T. D. *J. Chem. Phys.* **1989**, *91*, 3552. (c) Ditchfield, R. *Mol. Phys.* **1974**, *27*, 789.

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