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Transannular Orbital Interaction in Diketones Detected by C-13 NMR Spectroscopy

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Abstract: ^{13}C-NMR spectra of a series of acyclic, monocyclic and polycyclic ketones and diketones serve as a basis for investigating transannular orbital interaction in diketones. The shielding of the ^{13}C=O resonance frequency of the diketone relative to the monoketone which can be observed in all cases, depends on factors such as the number of intervening σ-bonds, relative orientation of the carbonyl groups and intervening σ-bonds.

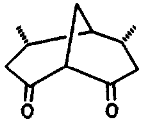
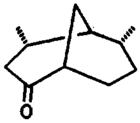
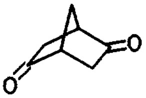
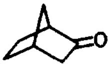
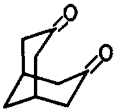
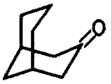
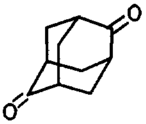
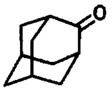
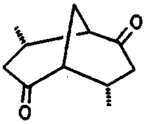
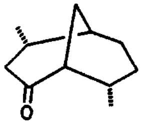
INTRODUCTION

Over 20 years ago Hoffmann described the phenomenon of electron delocalization through homoconjugation in terms of direct ("through-bond") and indirect ("through-space") interactions from localized chromophores.[2] Orbital interactions through space have been detected by photoelectron (PE)[3] and electron transmission spectroscopy,[3c,4] and by kinetics of solvolysis reactions.[5-7] For example, the large splittings of the π-orbitals (0.86 eV) and π^*-orbitals (1.52 eV) of norbornadiene, as detected by PE spectroscopy, are thought to originate mainly from through space interactions and to a lesser extent from through-bond coupling.[8] Transannular orbital interactions between two ketone carbonyl chromophores give large *n*-orbital splittings when overlap through skeletal σ-orbitals is possible, as in tetramethyl-1,3-cyclobutanedione (0.75 eV),[9] and smaller splittings arise when the overlap between the *n*-orbitals and the relevant σ-p ring orbitals is poor, as in 2,5-norbornanedione (0.16 eV).[10]

Although not as extensively investigated, transannular orbital interactions have also been detected by ^{13}C-NMR spectroscopy. With a favorable alignment of the C=O groups, $\delta_{C=O}$ of the dione may be strongly shielded relative to $\delta_{C=O}$ of the corresponding mono-ketone, *cf.* 2,5-norbornanedione ($\delta_{C=O}$ 212.3) and norbornanone ($\delta_{C=O}$ 218.1).[11] In the former, a 1,4-diketone, the chromophores are separated by three σ-bonds, but equivalently strong shieldings may be detected even in 1,5-diketones, where the

Dedicated to Professor Carl Djerassi on the occasion of his 70th birthday

TABLE 1. Influence of Homoconjugation on the ^{13}C-NMR Chemical Shifts[a] of Cyclic Ketones.

	Orbital Interaction Through n Bonds	Dione	$\delta_{C=O}$	Ketone	$\delta_{C=O}$	Δδ[b]	r(Å)[c]
(a)	2		203.3[d]		213.3[d]	-10.0	2.5[e]
(b)	3		212.3[f]		218.1[f]	-5.8	2.8
(c)	4		208.6[f]		212.5[f]	-3.9	3.0[g]
(d)	4		213.4[f]		218.3[f]	-4.9	3.5
(e)	4		208.9[d]		213.3[d]	-4.4	3.5[h]

[a] Measured in $CDCl_3$, δ in ppm downfield from $(CH_3)_4Si$.

[b] Dione minus ketone.

[c] Interchromophoric nonbonded distances from PCMODEL.

[d] Data from ref. 12. The methyl configuration is *endo* (R. Bishop, private communication).

[e] Order of stability from PCMODEL, kcal/mole (distance, Å): chair-chair, -92.72 (2.48); chair-boat, -88.94 (2.44); boat-boat, did not minimize.

[f] Data from ref. 11.

[g] Order of stability from PCMODEL, kcal/mole (distance, Å): chair-chair, -82.45 (2.97); chair-boat, -78.69 (3.58); boat-boat, -75.53 (4.05).

[h] Order of stability from PCMODEL, kcal/mole (distance, Å): chair-chair, -92.53 (3.50); chair-boat, -89.91 (3.39),; boat-boat, -85.22 (3.59).

chromophores are separated by four σ-bonds, as in bicyclo[3•3•1]nonane-3,7-dione ($\delta_{C=O}$ 212.5). The origin of the effect is thought to come mainly from through-space interaction.[11] Such transannular orbital interaction seems to be a general phenomenon, which occurs with and can be detected for other chromophores, *e.g.* in 3,7-dimethylenobicyclo[3•3•1]nonane($\delta_{C=CH_2}$ 145.2) compared with 3-methylene-bicyclo[3•3•1]nonane($\delta_{C=CH_2}$ 150.2).[11b]

In our earlier studies of transannular orbital interactions of diketones, detected by ^{13}C-NMR and PE spectroscopy,[12] orbital interaction was detected over 4 σ-bonds in bicyclo[3•3•1]nonane-2,6-dione, where the C=O groups are held in a favorable orientation (O=C···· C=O distance ≈ 3.5 Å). The dione $^{13}C=O$ resonance was strongly shielded ($\delta_{C=O}$ 212.5) compared with the monoketone ($\delta_{C=O}$ 216.9), but the *n*-orbital splitting was only modest (0.14 eV). In connection with those studies we initiated an investigation comparing diketone to corresponding mono-ketone $^{13}C=O$ chemical shifts for a series of cyclic ketones and their acyclic analogs where the intervening σ-bonds numbered from 2 to 5. In the following, we present and discuss those data.

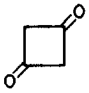
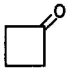
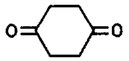
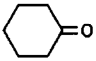
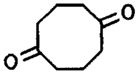
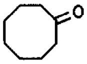
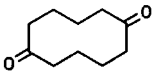
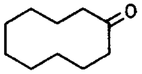
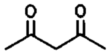
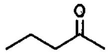
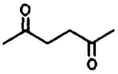
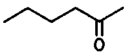
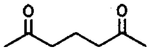
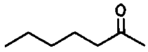
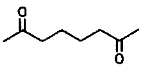
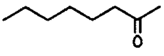
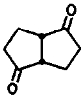
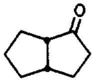
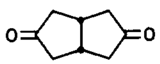
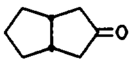
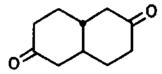
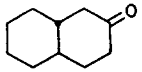
RESULTS AND DISCUSSION

Homoconjugative orbital interactions between two ketone carbonyl chromophores have been detected previously from studies of their C=O ^{13}C-NMR chemical shifts.[9,11-13] Several examples may be seen in Table 1, where the dione carbonyl carbon is shifted upfield from that of the parent monoketone. The source of the interaction may have its origins in through-space orbital interactions with the magnitude of Δδ being larger with the shorter distance between the carbonyl carbons (interchromophoric distance) [2.5 Å for (a), 3.5 Å for (e)]. Similar evidence for orbital interaction may be found in the diones of the current work.

Thus, as may be seen in Table 2, a large upfield shift is detected for the $^{13}C=O$ resonance of 1,3-cyclobutanedione (a) relative to that of cyclobutanone. The close proximity and favorable alignment of the two C=O groups in the dione suggest that a through-space interaction would make a major contribution to this effect, summarized as Δδ. In the diketone form of 1,3-cyclohexanedione, the C=O appears at 204.2 δ in $CDCl_3$. Here Δδ is -7.9 with the O=C···· C=O distance of 2.5 Å but also with a very different orientation of the C=O planes. When the O=C···· C=O distance is enlarged, as in 1,4-cyclohexanedione (b) and 1,5-cyclooctanedione (c), the magnitude of Δδ decreases. However, as might be expected, with an even larger O=C···· C=O, and perhaps with a less favorable transannular orientation, the magnitude of Δδ is much diminished, *e.g.*, in 1,6-cyclodecanedione (d). In 1,2-cyclohexanedione there is no evidence for the diketone form in $CDCl_3$, DMSO-d_6 or C_6D_6.

Orbital interaction through bonds undoubtedly contributes to the diketone $^{13}C=O$ shieldings seen in the monocyclic systems of Table 2. As a rough measure of this contribution, acyclic dione analogs of the monocyclic diketones were studied. Compare, for example, (a) and (e), both with two σ-bonds separating the carbonyl groups. The $^{13}C=O$ diketone resonance of (a) is more strongly deshielded than

TABLE 2. Influence of Homoconjugation on the ^{13}C-NMR Chemical Shifts[a] of Cyclic and Acyclic Ketones.

	Orbital Interaction Through n Bonds	Dione	$\delta_{C=O}$	Ketone	$\delta_{C=O}$	$\Delta\delta$[b]	r(Å)[c]
(a)	2		197.9		208.6[d]	-10.7	2.0
(b)	3		208.4		212.1	-3.7	2.9
(c)	4		213.2[e]		217.7[e]	-4.5	2.9
(d)	5		213.6[f]		214.4[d]	-0.8	4.8
(e)	2		202.2		209.0	-6.8	
(f)	3		207.1		209.4	-2.3	
(g)	4		208.4		209.4	-1.0	
(h)	5		208.7		209.4	-0.7	
(i)	3		220.3[g]		223.2[g]	-2.9	3.1
(j)	4		218.0		220.9[g]	-2.9	4.0
(k)	5		209.3[h]		209.2[h]	+0.1	5.3

[a] Measured in $CDCl_3$. δ in ppm downfield from $(CH_3)_4Si$. [b] Dione minus ketone. [c] Interchromophoric nonbonded (O=C···· C=O) distances from PCMODEL. [d] Cerichelli, G.; Frachey, G.; Galli, C. *Gazz. Chim. Ital.* **1986**, *116*, 683-686. [e] Bishop, R.; Lee, G-H. *Austral. J. Chem.* **1987**, *40*, 249-255. [f] House, H.O.; Lee, J.H.C.; VanDerveer, D.; Wissinger, J.E. *J. Org. Chem.* **1983**, *48*, 5285-5288. [g] Whitesell, J.K.; Matthews, R.S. *J. Org. Chem.* **1977**, *42*, 3878-3882. [h] Jones, J.B.; Dodds, D.R. *Can. J. Chem.* **1987**, *65*, 2937-2404.

that of (e), and the magnitude of $\Delta\delta$ is larger. Similarly, the magnitude of $\Delta\delta$ is larger in (b) than in (f), and larger in (c) than in (g). However, when the O=C···· C=O nonbonded distance becomes large, as in (d), $\Delta\delta$ is essentially the same as in its acyclic analog (h). Whether one can assign the difference in magnitudes of $\Delta\delta$ for the cyclic and acyclic analogs to through-space effects is unclear because of the difficulty in assessing the dependence of δ on the through-bond coupling path. However, on a qualitative basis, it seems clear that through-space effects play an important role in the ^{13}C=O shieldings of the cyclic diketones.

Through-space orbital interactions thus appear to be optimized in cyclic systems where the C=O groups have a favorable alignment. Compare $\Delta\delta$, for example, of the norbornanedione and adamantanedione [(b) and (d) of Table 1, respectively] to $\Delta\delta$ of cyclohexanedione and cyclooctanedione [(b) and (c) of Table 2, respectively]. In each case, the C=O groups are connected by three or four σ-bonds, but in the former set (Table 1) they are thought to be co-linear, and the magnitude of $\Delta\delta$ is larger. However, even with a favorable alignment, orbital interactions of diketones through the same three or four bonds do not necessarily give rise to very large $\Delta\delta$ magnitudes when there are intervening σ-bonds, even when the C=O are co-linear, as in (j), or when the C=O groups are not co-linear, as in (i).

CONCLUDING COMMENTS

The carbonyl resonances of all of the diones of this work (Table 2) are shielded relative to corresponding mono-ketones. This behavior is consistent with earlier observations in other bichromophoric systems with C=O chromophores aligned for transannular orbital interaction (Table 1).[11] The origin of this effect would appear to lie in orbital interaction through space as well as through σ-bonds. A more complete analysis of the relative contributions of through-space and through-bond orbital interaction awaits a theoretical analysis of ^{13}C=O shielding tensors[14] of the bichromophoric and monochromophoric substances of Tables 1 and 2.

EXPERIMENTAL

General. Nuclear magnetic resonance (NMR) spectra were determined in $CDCl_3$ on a GE QE-Plus spectrometer operating at 75.5 MHz for ^{13}C and are reported in parts per million downfield from tetramethylsilane, unless otherwise indicated. 1,3-Cyclobutanedione was a gift from LONZA Corp., 2-pentanone and 2,4-pentanedione, 1,4-cyclohexanedione and cyclohexanone, 2-hexanone and 2,5-hexanedione, cyclooctanone, 2-heptanone, 2-octanone and bicyclo[3•3•0]octane-3,7-dione were from Aldrich.

2,6-Heptanedione[15] was prepared according to the method of Cope and Overberger.[16,17]

2,7-Octanedione[18] was prepared according to the method of Januszkiewicz and Alper.[19]

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LONZA Corporation of Switzerland for a gift sample of 1,3-cyclobutanedione, and Professor H. Alper of the University of Toronto for the experimental procedure leading to 2,7-octanedione. Purchase of the NMR spectrometer at the University of West Florida was funded in part by a grant from the National Science Foundation's Instrumentation and Laboratory Improvement Program (Grant #USE-9050802).

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