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Experimental evidence at atomic resolution of intra- and intermolecular CO···π(arene) bond interactions☆

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Abstract

The crystal data of a number of carbonyl compounds have been reinvestigated. Interactions between carbonyl groups and π-arene systems have been more deeply discussed from a stereochemical point of view revealing the presence of stabilizing interactions. Preliminar ab initio calculations are in agreement with this interpretation. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

Intermolecular and intramolecular interactions of the type CO···π_{arene}, i.e. between the oxygen atom of a carbonyl group and the π electron cloud of an arene ring, have been experimentally deduced recently in a noticeable number of compounds [1–5]. It has also been suggested that these interactions may provide stability and/or have an important role in promoting chemical reactions albeit they involve relatively weak energies [2]. A computer search in crystallographic data files did not reveal a previous description of such interactions. Even though the corresponding geometrical parameters could be reported they have not been commented on, except for those furnished by our research group [1–4], so they seem to be the only ones mentioned so far in structural analyses. To our knowledge, one comparable interaction only, which however involves an imino group and a Cr-bonded CO, has been described [6]. Having judged that these features had not received adequate attention, we were prompted to reexamine a few structures in more detail and to expand the investigation into this unconventional type of interaction.

In this communication we describe this structural feature present in a series of compounds the crystal structure of which has been already published. These compounds are: *anti,syn*-bis-[$Cr(CO)_3$]$_2$-10-methyltribenzotriquinacene, **I** [1], *anti,anti,syn*-tris-[$Cr(CO)_3$]$_3$-10-methyltribenzotriquinacene, **II** [1], *anti,anti,anti*-tris-[$Cr(CO)_3$]$_3$-9*H*,10*H*-4*b*,9*a*-([1,2]benzenomethano)indeno-[1,2-*a*]indene, **III** [2], *anti,anti*-bis-[$Cr(CO)_3$]$_2$-9*H*,10*H*-4*b*,9*a*-([1,2]benzenomethano)indeno-[1,2-*a*]indene, **IV** [2], *anti,syn*-bis-[$Cr(CO)_3$]$_2$-9*H*,10*H*-4*b*,9*a*-([1,2]benzenomethano)indeno-[1,2-*a*]indene, **V** [2], *anti,-syn*-bis-[$Cr(CO)_3$]$_2$-4*b*,5,9*b*,10-tetrahydroindeno[2,1-*a*]indene, **VI** [3], *syn*-$Cr(CO)_3$-4*b*,9,9*a*,10-tetrahydroindeno[1,2-*a*]indene, **VII** [4], *anti,syn*-bis-[$Cr(CO)_3$]$_2$-4*b*,9,9*a*,10-tetrahydroindeno[1,2-*a*]indene, **VIII** [4], bis-

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☆ Dedicated to Professor Alberto Ceccon on the occasion of his 65th birthday.

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[phenyldiarylhydrazonecarbonyl]$_2$methylene, **IX** [5], and bis-[2-pyridyldiarylhydrazonecarbonyl]$_2$methylene, **X** [5]. The cases **I** through **VIII** are chosen as examples of intramolecular interactions of the type here discussed and are sketched in the Scheme 1, the cases **IX** and **X** are examples of intermolecular interactions.

2. Results and discussion

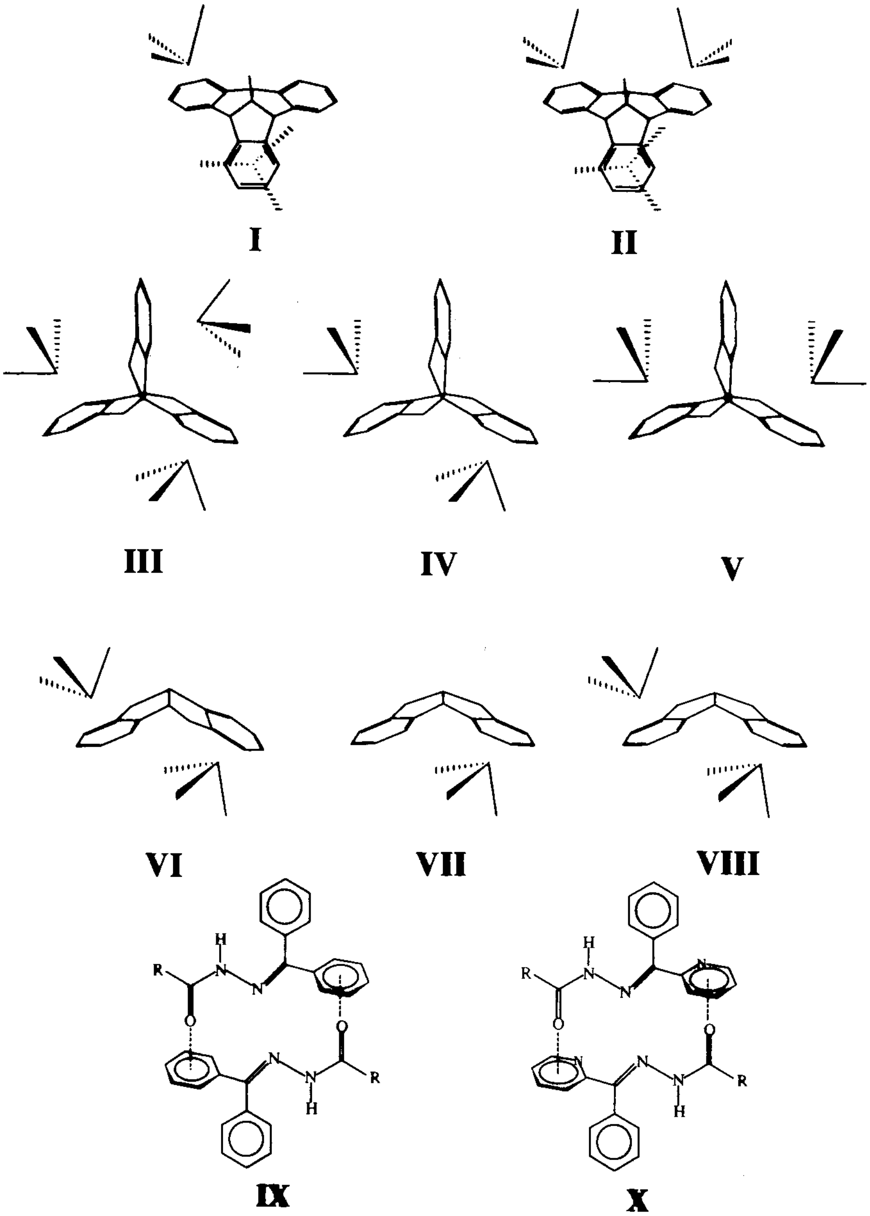
Table 1 reports for each compound listed in the Introduction the most relevant geometrical parameters concerning the structural feature here discussed, i.e. the distances between the carbonyl oxygen atom and the mean plane of the involved arene ring, the minimum and maximum distances from oxygen to the carbon atoms of the six membered ring of the arene, and the distance from the carbonyl carbon atom to the nearest carbon atom of the same arene ring.

In order to discuss these data a distinction must be made regarding the general aspect of the observed data.

Actually, we can distinguish the following main characteristics of the structural features here reported and shown in Scheme 2:

A, the–C≡O···arene interaction is established with arene groups already complexed with metals.

B, the –C≡O···arene interaction involves uncomplexed arene rings.



Scheme 1.

Table 1
Relevant geometrical parameters and the type of geometrical situation (see Scheme 2) for the compounds **I**–**X**

Compound	Type of structural situation	Distance (Å) from the $O_{C\equiv O}$ atom to Ph plane[a]	Distance(Å) from the $O_{C\equiv O}$ atom to the closest ring C atom	Distance (Å) from the $O_{C\equiv O}$ atom to the farthest ring C atom	Distance(Å) from $C_{C\equiv O}$ atom to the closest ring C atom	Reference
I	**A**	2.87	3.20	3.45	3.10	[1]
II	**A**	2.95	3.19	3.58	3.17	[1]
III	**A**	3.05 [a]	3.15 [a]	3.60 [a]	3.19 [a]	[2]
IV	**A**	3.09	3.30	3.56	3.27	[2]
V	**B**	3.20	3.45	3.60	3.29	[2]
	C	3.30	3.55	3.90	3.30	[2]
	C	3.22	3.45	3.45	3.20	[2]
VI	**A**	3.08	3.13	4.10	3.40	[3]
VII	**B**	3.25	3.43	3.80	3.30	[4]
VIII	**A**	3.08	3.40	3.40	3.26	[4]
IX	**D**	3.00	3.10	3.80	–	[5]
X	**D**	3.10	3.18	3.65	–	[5]

[a] These values are averaged among the three identical situations present in the same molecule.

C, the $-C\equiv O\cdots$arene interaction concerns arene groups facing in the opposite side another $-C\equiv O$ group.

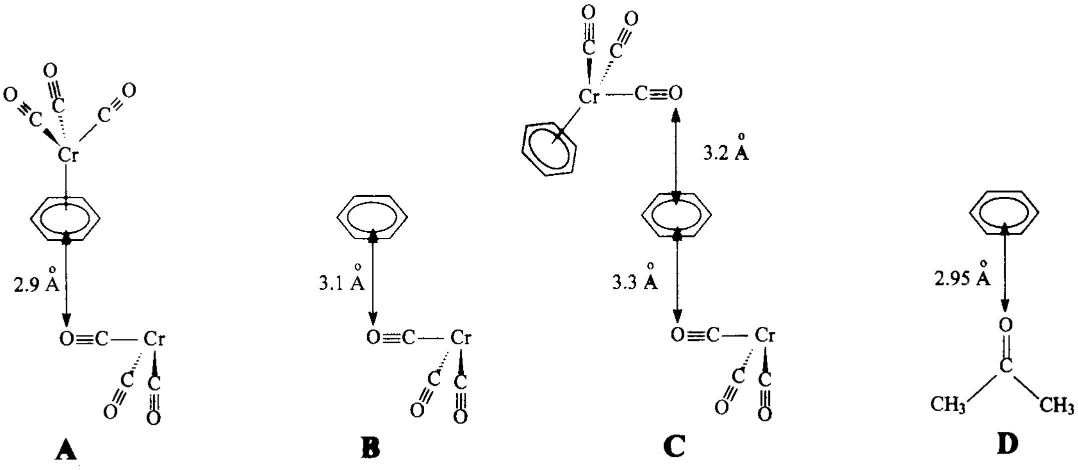
D, the arene ring interacts with ketonic $C{=}O$ groups.

In **A**, **B** and **C** the $-C\equiv O$ group belongs to a metal carbonyl and presents the $-C\equiv O$ axis almost parallel to the arene plane, in **D** the ketonic $C{=}O$ axis is nearly orthogonal to the arene plane. In Table 1 is indicated to which of these groups belongs each examined case.

Assuming that between the carbonyl groups and the aryl systems simply van der Waals interactions will establish, we calculate for the measured interatomic distances repulsion energies in the range of at least 1–5 Kcal/mole for O···Ph distances of ca. 3.3–2.9 Å, respectively. We used both potential energy formulas of Meson-Kreevoy [7] and Sheraga [8], obtaining quite similar results. The calculations are based on values of van der Waals radii given by Bondi [9] and Kitaigorodsky [10]. The ΔE values (reported in Table 1) are calculated considering the interactions of the carbonyl oxygen atom with all the carbon atoms of the involved six membered ring and the interaction of the carbonyl carbon atom with the nearest carbon atom of the same phenyl group, all the other distances being larger than 3.5–3.6 Å. These apparently unfavoured conformations could be easily avoided through a little rotation of the molecular moiety carrying the involved carbonyl group, as it can be easily proved using simple molecular models. On the contrary, these peculiar conformations seem even to induce other molecular constraints as observed in the case of **I**, **II** and **V**, where the $Cr(CO)_3$ tripods coordinated to the aryl six membered rings assume the quite unusual and certainly unfavoured eclipsed and/or *endo*-staggered conformations rather than the more usual *exo*-staggered [11] (see Scheme 3).

These facts lead us to surmise that in all these cases an attractive electron interaction takes place between the hybrid $-C\equiv O$ orbitals and the π-system; the corresponding bond energy should be at least equal, but more likely higher than the related repulsion energy. We believe that this is a consequence of a donor–acceptor interaction between CO and arene leading to a probable charge-transfer bonding. Actually, this effect is expected to be the more evident the higher is the polarization state of the arene six membered ring [12]. The situations **A**, **B** and **C** shown in Scheme 2 correspond to a decreasing order of a conceivable polarization of the arene ring, followed by an increase (as observed) of the $C\equiv O\cdots$Ph distances up to almost the disappearance of the effect in **C**. In **A** the polarization is stabilized by the coordination to the metal, in **B** it is provoked by induction of the facing $C\equiv O$ group; in **C** the competition effect of two $C\equiv O$ groups on opposite sides of the Ph ring almost inhibits its polarization, their distances from Ph are ca. 3.20 and 3.30 Å, respectively, revealing a non perfect mutual couterbalance with a probable residual bond interaction on one side.

All the cases indicated under types **A**, **B** and **C** here examined concern intramolecular interactions in which the $-C\equiv O$ groups belong to metal carbonyl moieties ($Cr(CO)_3$, in the reported cases). Quite different is the situation **D** shown in Scheme 2. The probable interaction is here of intermolecular nature, and $C{=}O$ belongs to ketone groups, thus characterized by a quite different electronic structure. In these cases the bond axis $C{=}O$ is nearly orthogonal to the phenyl rings and lay on the normal to their centers. No charge transfer is here conceivable, nonetheless a bond interaction must be still conjectured; the calculated repulsion energy, if of mere van der Waals nature, would be of ca. 1–2 kcal mol^{-1}. We think that also in these cases an electronic interaction takes place involving some degree of orbital



Scheme 2.

overlapping. It should be noted that significant contribution to the stabilization of self-assembled supramolecular networks in the solid state in cooperation with hydrogen bonds [5,13,14] can be just ascribed to these interactions.

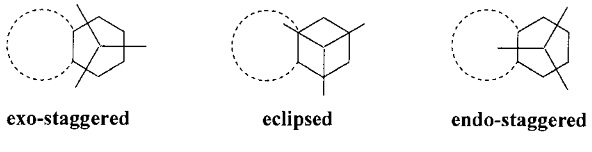
Further support to these hypotheses is provided by a series of ab initio calculations of single point energy for the model systems **A**, **B**, **C** and **D** of Scheme 2 with different distances among the component fragments. In particular, the geometry of each model has been approximated by averaging the structural data of the real molecular systems above quoted. In this preliminary investigation we have employed a standard Hartree–Fock method followed by second order Mollet–Plesset correction (HF-MP2) [16], using a minimal basis set STO-3G. In a few cases we have repeated the calculations using a STO-6G basis set obtaining equivalent results to within a few percent. The calculations have been performed using the software package GAMESS [17].

For each case we report in Table 2 the difference in energy between the configuration with fragments $Cr(CO)_3$ at a distance large enough to be considered infinite and the structures reported in the Scheme 2.

The results show that an attractive interaction between CO groups of the $Cr(CO)_3$ fragments and the arene group is operative in the cases **B** and **C**, yielding energies of -0.1 and 0.5 kcal mol^{-1}, respectively. In the cases **A** and **D** we obtain 1.5 and 0.2 kcal mol^{-1}. After subtraction of the van der Waals repulsive energies (vide infra) a residual attractive component results for **A**, **B**, **C** and **D** of -3.5, -3.1, -1.5 and -1.8 kcal mol^{-1}, respectively. We believe that the van der Waals energies we have calculated are likely to have been underestimated. In particular, in the case of **A**, the presence of a $Cr(CO)_3$ group η^6-coordinated to the arene ring probably imposes a more complete model. To this purpose, in an ongoing study we will refine the ab initio treatment accounting for the role of van der Waals forces in larger molecules employing (i) a pre-optimization of the geometry with the use of standard HF or even semi-empirical methods with an extended basis set, and (ii) a density functional theory (DFT) calculation of the total energy for the optimized geometry.

3. Conclusions

Using the X-ray diffraction structures of a number of compounds we were able to describe at atomic resolution intra- and intermolecular CO···π (arene) interactions. The reexamined structural data show that it is possible to establish a semiquantitative correspondence between the involved interatomic distances on one side and the hypothesized bond energy on the other side. More interestingly, the progressive variation of these distances (and thus of the corresponding energies) can be associated with a hierarchy of various chemical situations characterized by well defined physical properties (e.g. polarization effects on arene rings). It is also relevant that, due to these interactions, additional conformational constraints are caused and endured even if easily avoidable.



Scheme 3.

Table 2

Case	ΔE_{HF} [a]	$\Delta E_{v.d.W}$ [b]	ΔE_{attr} [c]
A	1.5	5	−3.5
B	−0.1	3	−3.1
C	−0.5	1	−1.5
D	0.2	2	−1.8

[a] ΔE_{HF} is the calculated [15,16] difference in energy between the configuration with the $Cr(CO)_3$ fragments at infinite distance and at their distance reported in Scheme 2.

[b] $\Delta E_{v.d.W.}$ is the van der Waals repulsion calculated with the potential energy formulas of Meson-Kreevoy [7] and Sheraga [8].

[c] $\Delta E_{attr.} = \Delta E_{HF} - \Delta E_{v.d.W.}$.

We conclude that in all the cases **A**, **B**, **C** and **D** the CO···π-arene interactions are very likely attractive and can reasonably be described as unconventional bond interactions probably of charge-transfer bonding type in which donor–acceptor energy and/or polarization energy [15] do exceed the van der Waals repulsion energy; they are also controlled by geometrical factors such as the orientation of the CO groups with respect to the arene plane. Preliminary theoretical calculations agree mostly with these conclusions.

4. Material and methods

As mentioned in the Introduction, the crystal data are those reported in the quoted references. Ab initio calculations have been performed on a DEC Alpha 3000/200 workstation using GAMESS [17], and adopting a standard HF method with STO-3G and STO-6G basis, followed by second order Moller–Plesset perturbation correction [16].

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