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Weak Interactions

The Experimental Observation of the Intramolecular NO_2/CO Interaction in Solution**

*Michel Chiarucci, Alessia Ciogli, Michele Mancinelli, Silvia Ranieri, and Andrea Mazzanti**

Abstract: *The weak electrostatic interaction between nitro and carbonyl moieties has been observed by means of variable-temperature NMR spectroscopy. Its energetic contribution was evaluated to be about 3 kcal mol^{-1} by DFT calculations, and confirmed by the measurement of internal energy barriers to the rotation of suitable nitroaryl rings.*

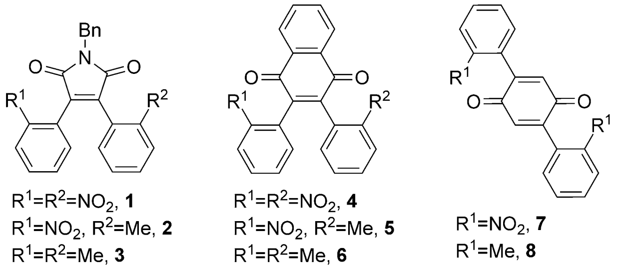
Weak chemical interactions play a key role in chemistry. They are effective in many biological systems, and they can be employed to design supramolecular assemblies and scaffolds.[1] Among them, hydrogen bonds,[2] halogen–halogen bonds,[3] and van der Waals dispersive forces[4] are the most studied labile interactions. Salt bridges are well-known to drive protein folding and stability,[5] and electrostatic π–π interactions have been extensively studied from a theoretical point of view.[6] Recently, it was shown that noncovalent interactions can modulate the conformational preferences and stereoselectivity of some organocatalysts.[7]

Some years ago, it was shown that a weak bond due to the electrostatic interaction between nitrogen and oxygen was responsible for the stabilization of the crystal structure of *N*,*N*-dipicrylamine,[8] and that the intermolecular N–O interaction was one of the driving interactions for the self-assembly of *N*-oxalyl-2,4-dinitroanilide in the solid state.[9] Through-space interactions were also observed in the solid state for a series of bipyridine *N*-oxides.[10] Ab initio calculations[11] had suggested that the energy involved in the N–O interaction was about 13 kJ mol^{-1}.

We thus speculated that the weak interaction between a nitro and a carbonyl group could compete with other weak interactions in the stabilization of preferred molecular conformations in the solid state, as well as in solution, provided the correct geometries of the two acting partners are met. Herein we report the first experimental observations of this weak interaction in solution, and a quantitative measurement of its strength.

The design of a chemical system suitable for the observation of this interaction should consider the potential of the two acting parts (i.e., the carbonyl and the nitro group) to move at a great amplitude without significant variation of the overall conformational energy, to enable the best geometry for maximum stabilization to be adopted. Such a situation can be found in biaryl systems, in which the energy minima are known to be quite flat.[12] At the same time, the chemical system should generate two different conformations that can be observed by dynamic NMR spectroscopy.

We recently reported that bisaryl maleimides (Scheme 1) yield atropisomers when highly hindered aryl systems are bound to the 3,4-positions[13] because of the out-of-plane disposition of the two aryl rings. When less-hindered *ortho*-substituted aryl systems are bound to the 3,4-positions of maleimide, the rotational barriers are smaller; nevertheless, they could be detected by dynamic NMR spectroscopy.[14] We envisaged that this particular system fulfilled the required features for us to study the intramolecular NO_2/CO interaction.



Scheme 1. Structure of the compounds used in this study. Bn = benzyl.

DFT computational studies and dynamic NMR spectroscopic data showed that the energies of the *syn* and *anti* conformers were very similar when aliphatic *ortho*-aryl substituents were employed, despite the differences in the steric requirements in the ground states and the huge range of experimental interconversion barriers (12.9–26.0 kcal mol^{-1}).[13] In contrast, the same calculations suggested that in the case of compound **1**, which bears two *o*-nitrophenyl groups, the *anti* conformer was more stable than the *syn* conformer by more than 4 kcal mol^{-1} (at the B3LYP/6-31G(d) level), thus implying that only the *anti* conformer should be populated. From a steric point of view, the nitro group is very similar to the methyl group;[15] thus steric considerations cannot explain the large stabilization of the *anti* conformation. Calculations at the B3LYP/def2-TZVP, B97D/def2-TZVP, ωB97XD/def2-TZVP, and ωB97XD/6-311++G-

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(2d,p) levels confirmed the large stabilization of the *anti* conformer with respect to the *syn* conformer (see Table 1). A bias due to the previous theoretical approach seems therefore to be unlikely.

Table 1: Summary of calculations.[a]

Compd	Level of calculation	ΔH° [kcal mol^{-1}][b]	*anti*/*syn* (exptl)
1	B3LYP/6-31G(d)	4.1	>99.5:0.5
1	B3LYP/def2-TZVP	4.0	
1	B97D/def2-TZVP	2.6	
1	ωB97XD/def2-TZVP	3.3	
1	ωB97XD/6-311++G(2d,p)	3.0	
2	ωB97XD/6-311++G(2d,p)	−0.6	21:79[c]
3	ωB97XD/6-311++G(2d,p)	−0.2	45:55[d]
4	B3LYP/def2-TZVP	4.6	>99.5:0.5
4	ωB97XD/def2-TZVP	4.0	
4	ωB97XD/6-311++G(2d,p)	4.0	
5	ωB97XD/6-311++G(2d,p)	1.1	68:32[c]
6	ωB97XD/6-311++G(2d,p)	0.4	59:41[c]
7	ωB97XD/6-311++G(2d,p)	0.9	67:33[e]
8	ωB97XD/6-311++G(2d,p)	0.7	58:42[e]

[a] All calculated energies are ZPE-corrected enthalpies (ZPE = zero-point energy). [b] A negative value means that the *syn* conformation is calculated to more stable than the *anti* conformation. [c] The ratio was determined from the NOE NMR spectrum. [d] Ref. [13]. [e] The ratio was assigned on the basis of calculations.

A close examination of the optimized structures showed that, on each side of the maleimide ring, an electrostatic interaction took place between the electron-rich oxygen atom of the carbonyl group and the nitrogen atom of the nitro group. A second electrostatic interaction was present, with reverse polarity, between one of the oxygen atoms of the nitro group and the electron-poor carbon atom of the carbonyl group (Figure 1). The calculated distance between the oxygen atom of the carbonyl group and the nitrogen atom was very similar to that observed for *N*-oxalyldinitroanilide (2.85 Å), although in that case the interaction was intermolecular and in the solid state.[2c,9] Such an interaction could also take place in the *syn* conformer, but in this case only one stabilizing interaction could be effective, because the second interaction would drive the opposite sides of the phenyl rings close to each other, thus generating a destabilizing steric clash.

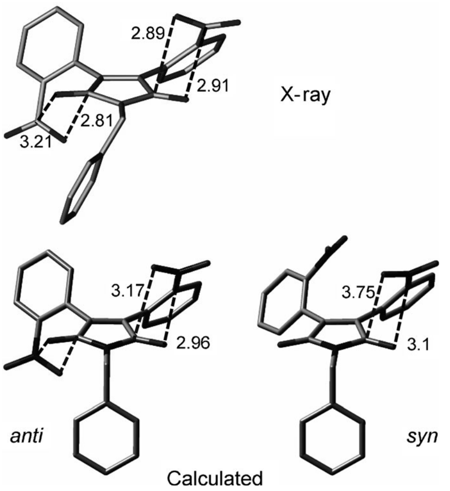


Figure 1. Top: X-ray crystal structure of compound **1**. Bottom: calculated structures of the *anti* and *syn* conformers at the ωB97XD/6-311++G(2d,p) level. Distances in Å.

Compound **1** was crystallized from a solution in acetonitrile, and the solid-state structure fully confirmed the hypothesis of the calculations. Only the *anti* conformer is present in the centrosymmetric unit cell, and both nitro groups interact with the two carbonyl groups.[16] In each case, the oxygen atom of the carbonyl group lies exactly orthogonal to the plane of the nitro group; thus, the electrostatic interaction of the electron-rich oxygen atom with the electron-poor nitrogen atom is possible, as well as the interaction of one oxygen atom of the nitro group with the carbon atom of the carbonyl group. The N–O and O–C distances are very similar to those reported.[8] The skew angles of the two *o*-nitrophenyl rings were calculated to be −57°, whereas the experimentally found angles were −49° and −55°.

To determine whether this interaction could also be observed experimentally in solution, we acquired variable-temperature NMR spectra. When a sample of **1** in $CDCl_3$ was cooled to −24 °C, the broad signal of the benzylic CH_2 group was split into an AB system, and no signals ascribable to a second conformer could be detected (Figure 2). This result implies that the rotation of the *o*-nitrophenyl groups was frozen and that the single observed conformation did correspond to the *anti* geometry (C_2 symmetry).[17] The racemization barrier due to rotation of the *o*-nitrophenyl rings was derived by lineshape simulation as 14.2 ± 0.2 kcal mol^{-1}. This value is matched very well by the value of 14.3 kcal mol^{-1} found by DFT calculations (or 13.5 kcal mol^{-1} if the ZPE-corrected enthalpy is considered).

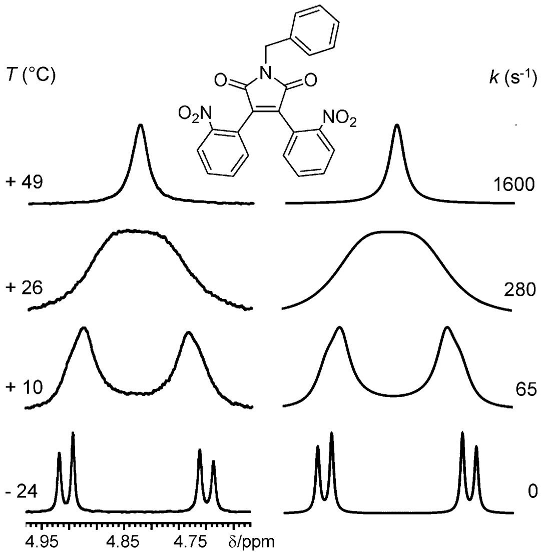


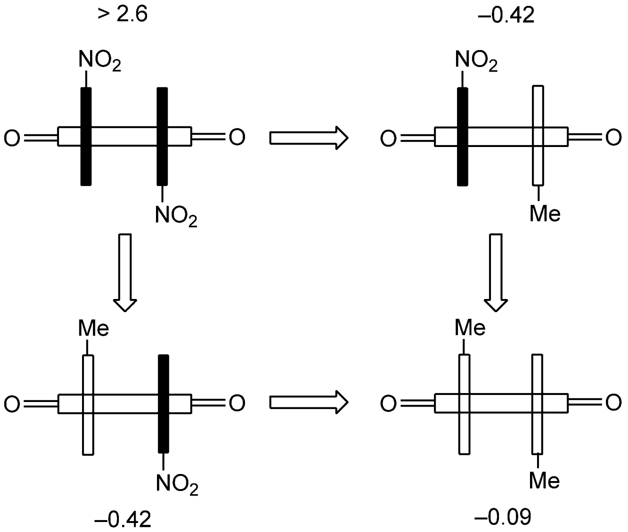
Figure 2. Variable-temperature ^1H NMR spectra of **1** (600 MHz in $CDCl_3$). Left: experimental spectra. Right: simulated spectra with the relative rate constants.

The absence of the *syn* conformer at −24 °C provided suitable information about the stabilization energy involved in the electrostatic interactions. If a 99.5 : 0.5 ratio at −24 °C is taken into account,[18] the corresponding energy difference ($\Delta G°$) is 2.6 kcal mol^{-1}. This value is the lower limit for the stabilization of the *anti* conformation because the *syn* conformer was not detectable at all. As one NO_2/CO interaction is available in both conformations, the value should be considered a direct measurement of the strength of the electrostatic interaction. The value nicely matches the DFT-predicted value (2.6 ± 4.1 kcal mol^{-1}; see Table 1).[19]

For the following considerations, it should be taken into account that the electrostatic interaction shrinks the dihedral angle between the maleimide and *o*-nitrophenyl rings towards the geometry of the transition state, in which the aryl ring is coplanar to the maleimide ring. At the same time, the motion of one ring towards the transition state forces the second ring to become perpendicular with respect to the maleimide plane, to minimize the steric interaction between the two rings (see Figure S1 in the Supporting Information). The displacement of the second ring weakens the NO_2/CO interaction, and the observed energy barrier is the result of the sum of these two contributions (i.e. the steric clash between the rotating ring and the maleimide ring, and a partial loss of the NO_2/CO stabilization for the second ring).

Having found an example for which the electrostatic interaction can be observed, we searched for more examples and for a quantitative evaluation of its energetic contribution (Scheme 1). Compound **2** bears one *o*-nitrophenyl and one *o*-tolyl ring. Whereas the nitro group can be involved in the NO_2/CO interaction, the disposition of the *o*-tolyl ring is driven only by steric factors. Indeed, the low-temperature NMR spectrum of **2** at −41 °C in $C_2D_2Cl_4$ (see Figure S2) showed that both conformations were populated in a 71:29 ratio, and NOE spectra showed that the *syn* conformation was the more populated conformation (see Figure S3).[20] The ^{1}H methyl signal is split only when the two conformers are generated; thus, it indicates the smaller of the two rotational barriers of the two aromatic rings. On the other hand, the CH_2 group is a chirality probe that indicates the formation of the enantiomeric pair generated by the frozen rotation of the ring with the higher rotational barrier. The simulation of the methyl signal provided a value of 12.6 ± 0.2 kcal mol^{-1} for the *syn*/*anti* interconversion, and the energy barrier derived from the simulation of the benzylic CH_2 group was very similar (12.9 ± 0.2 kcal mol^{-1}; see Figures S4 and S5).[21] The equivalent rotational barriers confirmed that the methyl and nitro groups are isosteric,[15,22] and the reliable assignment of the two measured barriers is impossible. Nevertheless, both barriers are significantly lower than that of compound **1**, thus confirming a substantial contribution to the ground-state stabilization in the case of **1**. Similarly, we found for compound **3** a *syn*/*anti* ratio of 55:45, equivalent to $\Delta G° = 0.09$ kcal mol^{-1} (see Figure S6).

Having established the experimental ratio of the two conformations of **2** and **3**, we could evaluate the energetic contribution of the electrostatic interaction by using compounds **1**–**3** as the components of a chemical double-mutant cycle (DMC),[4c,23] in which compounds **2** and **3** are the single and double mutant with respect to compound **1** (Scheme 2). By using this approach and the lower energy-difference limit determined for **1** (i.e. 2.6 kcal mol^{-1}), we calculated that the stabilization due to the electrostatic interaction corresponds to 3.35 kcal mol^{-1}.



Scheme 2. DMC cycle for compounds **1**–**3**. The indicated values (in kcal mol^{-1}) are the energy differences ($\Delta G°$) between the *anti* and *syn* conformers as measured by NMR spectroscopy at −40 °C. Negative values indicate that the *syn* conformation is more stable than the *anti* conformation.

To check whether the NO_2/CO interaction was restricted to the geometric constraints of the pentaatomic scaffold of maleimide, we prepared compounds **4**–**6** containing the 1,4-naphthoquinone scaffold. Within this series, the *anti* conformer of compound **4** should gain stabilization from two NO_2/CO interactions, whereas in compounds **5** and **6**, both conformers should be populated. DFT calculations at the B3LYP/def2-TZVP, ωB97XD/def2-TZVP, and ωB97XD/6-311++G(2d,p) levels suggested that in the case of compound **4**, the *anti* conformer was more stable than the *syn* conformer by at least 4.0 kcal mol^{-1} (Table 1), whereas for **5** and **6**, the two conformers were calculated to be very close in energy.

The ^{1}H NMR spectrum of **4** at +25 °C showed a single set of signals, whereas the spectra of **5** and **6** revealed the presence of both the conformers in a 68:32 and 59:41 ratio, respectively. The *anti* conformation was confirmed in both the latter compounds to be the more abundant on the basis of NOE spectra (see Figures S8 and S9). The energy barriers for the *o*-nitrophenyl rotation were calculated for compounds **4** and **5** as 22.7 and 22.3 kcal mol^{-1}, respectively, and as 21.0 kcal mol^{-1} for the *o*-tolyl rotation in **6.** As they are inaccessible for the dynamic NMR spectroscopic technique, the energy barriers for compounds **5** and **6** were determined by 1D EXSY, which yielded barriers of 21.0 ± 0.2 and 20.7 ± 0.2 kcal mol^{-1}, respectively (see Figure S10). Thus, in the case of **4**, the ambient-temperature NMR spectrum should display the presence of a second conformation, if it were populated.

The absence of a suitable chirality probe did not allow the determination of whether the single conformer observed in the NMR spectra of **4** corresponded to the *anti* or to the *syn* conformer. X-ray diffraction showed that only the *anti* conformer was present in the solid state, with NO_2/CO distances and geometries very similar to those in compound **1** (see Figure S7). The ambient-temperature ^{1}H NMR spectrum recorded in a chiral environment[24] showed the splitting of some aromatic signals, thus confirming that the *o*-nitrophenyl rotation was frozen. Unfortunately, the observed splitting did not allow the unambiguous assignment of the *anti* geometry to the single observed conformation because the signals of the *syn* conformer would also be split by the enantiomerically pure environment.[25]

Compound **4** was therefore analyzed by enantioselective HPLC, which showed two peaks undergoing dynamic exchange at +25 °C. At 0 °C, the two chromatographic peaks were well-resolved, and electronic circular dichroism (ECD) at 280 nm showed that they had opposite sign (Figure 3). Thus, we were able to unambiguously confirm the presence of solely the enantiomeric pair of the *anti* conformation, and also to evaluate the racemization barrier as 20.5 ± 0.3 kcal mol^{-1} by means of dynamic HPLC[26] (see Figure S11). By applying the same approach used for **1** to the case of compound **4**, we determined that the stabilization energy of the *anti* conformation has to be larger than 2.6 kcal mol^{-1}. The application of the DMC approach to the present situation (compounds **4**–**6**) then yielded a lower limit of 1.9 kcal mol^{-1} for the stabilization energy.

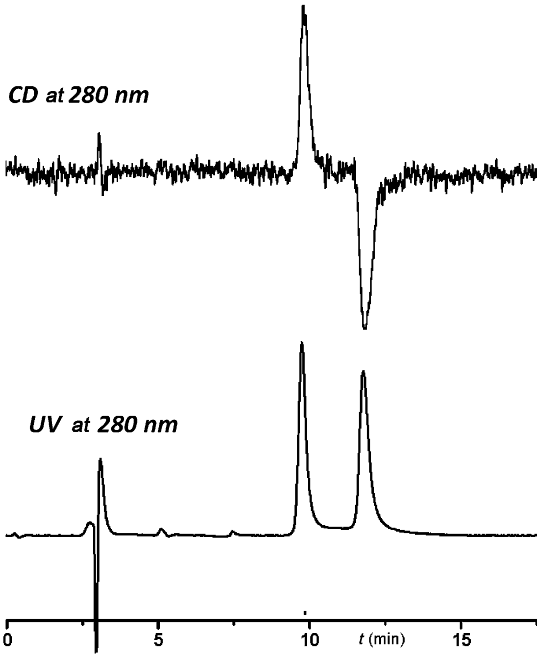


Figure 3. Chromatograms of compound **4** on an enantioselective (*R,R*)-Whelk-O1 HPLC column, recorded at 0 °C. Bottom trace: UV detector. Top trace: ECD detector at 280 nm.

As a final attempt to experimentally measure the electrostatic interaction without any interference caused by the proximity of the aryl rings, we prepared compounds **7** and **8**. The 1,4-benzoquinone scaffold of compound **7** bears two *o*-nitrophenyl rings in the 2,5-positions; hence, their rotations are completely independent. Nevertheless, two NO_2/CO interactions can be effective, and the ground state of both the *syn* and *anti* conformers can be stabilized in the same way by the electrostatic interaction. Compound **8** shares the same situation, but the rotational barrier is now driven only by steric effects. The transition states for the aryl-ring rotation correspond to a geometry in which the *ortho* substituent of the rotating ring is close to the hydrogen atom in the 3-position (or 6-position), and the *syn*/*anti* interconversion needs the rotation of only one ring. As the nitro and methyl moieties are isosteric, the barrier for rotation is mainly due to the stabilization of the ground state.[27] Thus, the rotational energy *difference* for the *syn*/*anti* interconversion between **7** and **8** has to be assigned to the stabilization due to a single NO_2/CO interaction. At −65 °C, the ^{1}H NMR spectrum of **7** showed that both conformations were populated in a 67:33 ratio, whereas the spectrum of **8** at −118 °C showed a 58:42 ratio (see Figures S12 and S13). The energy barrier for the *syn*/*anti* interconversion of **7** was found to be 12.0 ± 0.2 kcal mol^{-1}, whereas the barrier for **8** was found to be 9.1 ± 0.2 kcal mol^{-1}. Thus, the stabilization due to a single NO_2/CO interaction was evaluated to be 2.9 kcal mol^{-1}, in agreement with the previous considerations.

In conclusion, we have documented the observation of the weak NO_2/CO electrostatic interaction in solution. The energetic contributions were established by means of DFT calculations and dynamic NMR spectroscopy, and by the use of the DMC approach. Further investigations on other chemical systems potentially suitable for gaining a deeper understanding of this interaction are currently in progress.

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[20] In this case, the benzylic CH_2 group corresponded to an AB system for both conformers, and the major conformer was assigned as *syn* on the basis of NOE experiments (see the Supporting Information).

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[27] The small difference in the observed conformer ratio between **7** and **8** could stem from different interactions with the solvent.

Communications

Weak Interactions

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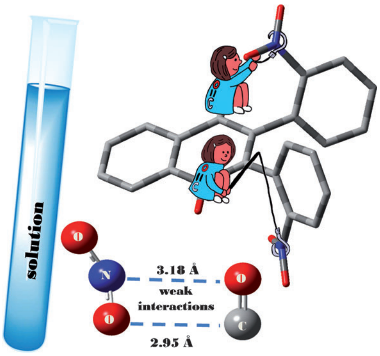
The Experimental Observation of the Intramolecular NO_2/CO Interaction in Solution



Might without muscle: The weak electrostatic interaction between nitro and carbonyl moieties has been observed by means of variable-temperature NMR spectroscopy. Its energetic contribution was evaluated to be about 3 kcal mol^{-1} by DFT calculations, and confirmed by the measurement of internal energy barriers to the rotation of suitable nitroaryl rings (see picture).