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Weak donor-acceptor intermolecular interactions under pressure: the $NO_2\cdots NO_2$ case.

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The importance of weak intermolecular interactions in crystals is widely acknowledged in crystal engineering, but it is also relevant for topics like physical organic chemistry, drug design, protein folding, enzymatic reactions, and supramolecular chemistry. However, at times, the specific role played by particular interactions may be not fully understood. [1]
In the quest for increasing our knowledge on the plethora of intermolecular interactions in crystals, high pressure can be a remarkable probing tool, allowing us to extract valuable information on the compressibility of different interactions and thus helping to clarify the role of different interactions for crystal packing. Moreover, at extreme conditions these interactions may induce polymorphism or even chemical reactions, although they may be not so relevant role for the cohesion at ambient conditions.
The best known and well characterized of such interactions is the ubiquitous hydrogen bond, but, recently, also the so-called "halogen", "chalcogen", and even "carbon" bond have aroused growing interest. At present, however, other kinds of weaker interactions have not been so deeply investigated. Nevertheless, for a better understanding of the effect of intermolecular interactions on material properties, there is a strong need of comparing simultaneously different interactions and establish their hierarchy. A unifying scheme for all intermolecular interactions is therefore desirable; a viable option could be classifying them as incipient electron donor-acceptor interactions within the solid paradigm of frontier molecular orbitals, where every interaction is seen as an overlap between the HOMO of the electron donor and the LUMO of the acceptor. [2]
In this study, we focused our attention on unusual $\pi^*\leftarrow n$ interactions between NO_2 groups. Although these interactions are not very well known, more than 4000 structures in the Cambridge Structural Database contain contacts between oxygen and nitrogen atoms from nitro groups that are shorter than the sum of the Van der Waals radii. The nature of this interaction is at present still controversial. While some earlier studies classified it as repulsive, others claimed that $NO_2\cdots NO_2$ interactions are attractive, and comparable in energy to weak hydrogen bonds. [3] Furthermore, several conformations are possible, in which the NO_2 groups can lie on parallel or perpendicular planes. In the former case we can further distinguish between syn and anti conformations, while in the latter we have four possibilities: syn-periplanar, syn-clinal, anti-clinal, and anti-periplanar.

The crystal structure of 4-amino-4'-nitrobiphenyl was studied at high pressure with XRD experiments and ab initio and periodic-DFT calculations. A previously unreported polymorph was observed as a consequence of a pressure induced phase transition that seems to maximize the contact between NO2 groups. High pressure periodic DFT calculations were also performed on other two systems containing several $NO_2\cdots NO_2$ contacts: 1-hydrazino-2,2-dinitroethenamine, and on 3-nitrato-1-nitroazetidine.
In order to analyze the observed results and to better classify the nature of this unusual interaction, we have adopted some theoretical tools, like pairwise atomic potential energies and forces, modelling of idealized $NO_2\cdots NO_2$ dimeric models with different configurations, and electron density analysis with Fukui functions.
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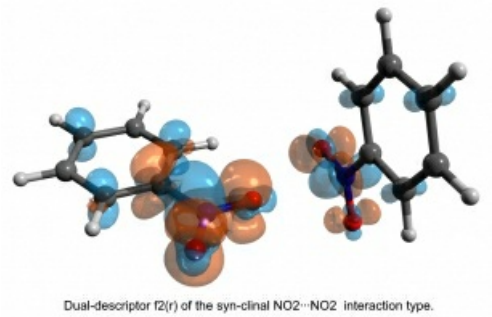

Dual-descriptor f2(r) of the syn-clinal NO2···NO2 interaction type.

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