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The first observation of nitrogen–carbonyl bonding: self-assembly of *N*-oxalyl 2,4-dinitroanilide assisted by a weak N···O=C interaction†

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A new type of weak bond, *i.e.*, the N···O=C interaction, that determines the crystal packing of *N*-oxalyl 2,4-dinitroanilide (1) in cooperation with C–H···O hydrogen bonds, has been found and is rationalized by *ab initio* calculations as being the result of electrostatic interactions.

Weak inter- or intra-molecular interactions play a crucial role in many biological systems and can be utilized to design materials with desired physical and chemical properties.[1] Weak interactions, which lead to the formation of complex and highly structured macroscopic assemblies, have been well documented. Among them, the O(N)–H···O(N),[2] C–H···O(N)[3] and X···X (where X is Cl, Br, S, Se, *etc*.)[4] types of contacts are the most well known examples of such weak interactions. However, *ab initio* calculations revealed that the energy of the N···O interaction is 10 ~ 13 kJ mol^{-1},[5] which is close to the energies of C–H···O and C–H···N hydrogen bonds, and so the N···O interaction should be strong enough to compete with other types of weak interactions in the formation of supramolecular structures. Indeed, it was shown that the N···O interaction between the two nitro groups in *N*,*N*-dipicrylamine and its ionic complexes did play an important role in stabilizing its crystal structure.[6] However, this nitro–nitro type N···O interaction is the only example reported so far in the literature. Herein, we wish to report a new type of N···O interaction formed between the carbonyl oxygen and nitro nitrogen in the crystal structure of *N*-oxalyl 2,4-dinitroanilide (**1**). This new N···O weak bonding, in cooperation with other types of weak interaction (*i.e.*, the C–H···O hydrogen bond), plays an important role in the self-assembly of this molecule in the solid state. *Ab initio* calculation of charge distribution confirmed that the N···O=C contact mainly resulted from electrostatic interactions between the partially positively charged nitrogen of the nitro moiety and the partially negatively charged oxygen of the carbonyl. Furthermore, the calculated individual N···O=C interaction energy indicates that this kind of weak interaction is fairly strong and should make a significant contribution to stabilizing the crystal packing.

Compound **1** was synthesed by coupling 2,4-dinitroaniline with 3.0 equiv. of oxalyl chloride in CH$_2$Cl$_2$ solution, and then adding methanol. The resultant solution was vacuum dried and the residue purified by column chromatography to give **1** in 75% yield. Crystals of **1** were obtained from a mixture of ethyl acetate and petroleum ether (bp 60–90 °C).‡

In the solid state, the only conventional hydrogen bond donor, NH, was involved in forming an intramolecular hydrogen bond with a neighboring oxygen of the nitro moiety as expected (the N–H···O distance is 2.571 Å and the bond angle is 134.6°). This prevents NH from engaging in crystal packing. There are two kinds of C–H···O hydrogen bonds involved in the crystal packing of **1** (Fig. 1, part A and B in e): The two parallel C–H···O hydrogen bonds with an H···O distance of 2.351 Å and a C–H···O angle of 129.4° compose one kind of C–H···O hydrogen bond, which has the role of forming a **1·1** dimer (Fig. 1, a).The other one is in a branching trimer **1·1·1** with an H···O distance of 2.564 Å and a bond angle of 176.5° (Fig. 1, b). Although the first kind of C–H···O hydrogen bond found in the **1·1** dimer is shorter than the H-bond in the **1·1·1** trimer and this should result in a smaller bond angle because short C–H···O hydrogen bonds tend to be more linear.[3] A more linear C–H···O hydrogen bond was not observed in the **1·1** dimer, probably due to the geometric constraints of the C–H orientation. On the other hand, the second kind of C–H···O hydrogen bond is an average one. Cooperation of these two kinds of hydrogen bonds determines the layer structure of **1** in the pillar-halves (Fig. 1, e).

Besides hydrogen bonding, a novel N···O=C interaction was detected in the crystal packing of **1**, which fills the role of bridging the two pillar-halves to form the three-dimensional structure of **1** (Fig. 1, c). The N···O distance is 2.852 Å, which is shorter than the sum of the van der Waals radii.[7]

It is well known that direct interactions formed by halogens with NO$_2$ groups are polarization-induced.[8] In the cases of N···S, S···S, and S···Cl contacts, polarization effect was also found to be an important factor.[1] However, the hardness of N and O atoms are both high, and so they cannot be readily polarized. Therefore, the formation of the N···O=C interaction reported herein can hardly be attributed to a polarization factor. Wozniak *et al*.[6] considered that the N···O interaction in *N*,*N*-dipicrylamine should result from electrostatic interaction between the partially positively charged nitrogen atom in one nitro group and the partially negatively charged oxygen atom in another nitro group. Similarly, the N···O=C interaction may

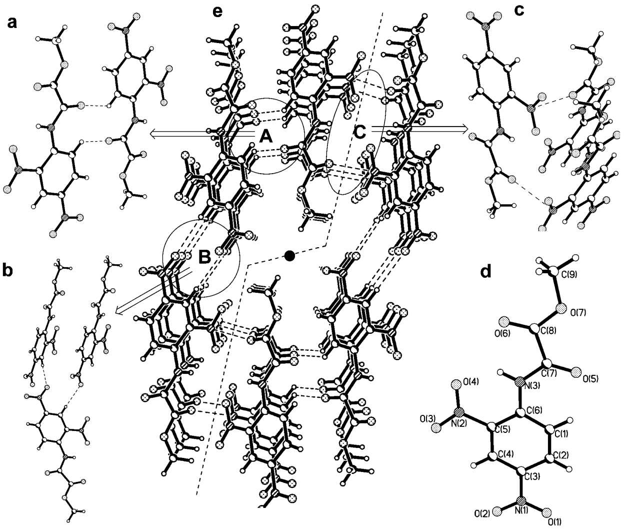

Fig. 1 Intermolecular interaction network of the two pillar-halves in the crystal packing of **1**. (a) **1·1** dimer formed by two parallel C–H···O hydrogen bonds (H···O distance 2.351 Å, C–H···O angle 129.4°) (top view of A); (b) **1·1·1** trimer formed through the nearly linear C–H···O hydrogen bonds (H···O distance 2.564 Å, C–H···O angle 176.5°) (side view of B); (c) N···O=C interaction between the two pillar-halves (N···O distance 2.852 Å) (side view of C); (d) molecular structure and atomic numbering scheme of **1**; (e) crystal packing of **1** (viewed down the crystallographic *b*-axis).

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† Electronic supplementary information (ESI) available: synthesis details and spectroscopic data for **1**. See http://www.rsc.org/suppdata/cc/b3/b306012h/

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also result mainly from electrostatic interaction due to the fact that the carbonyl oxygen in **1** is also negatively charged.

To address the nature of the N···O=C interaction, we cut out mono- and tri-molecule units as models of configuration in the crystal. At the HF/6-31G* and HF/6-31G** levels, the Mulliken population analysis has been carried out on the geometries of mono- and tri-molecule units using the Gaussian 98 program. Only the representative results of charge distribution of mono-molecules have been illustrated in Fig. 2 because the analyzed results at these two levels were similar. As can be seen from Fig. 2, O(6) (the no. of the atom is the same as shown in d of Fig. 1) carries the largest negative charge (−0.548) and N(2) carries a quite high positive charge (0.504). The charges of N(2) and O(6) in the tri-molecule are 0.544 and −0.582, respectively. From the charge distribution calculation, it is demonstrated again that the formation of an N···O=C interaction should be mainly attributed to electrostatic interactions. In addition, the geometry of the N···O bond is found to be vertical to the plane of nitro that could mostly reduce the repulsion of the highly negatively charged carbonyl oxygen and nitro oxygen between two molecules of **1**. It is also noted that the protons of the phenyl ring and amide group all bear a high positive charge, and therefore make them suitable for hydrogen bond interactions.

Stabilization energy resulting from N···O=C interactions in the **1·1·1** trimer (Fig. 1, c) was computed as the difference in energy between the trimer and three isolated monomers.[9] At the HF/6-31G* level, the calculated stabilization energy within the trimer is −6.6 kcal mol^{-1}. After removing the energy of π–π stacking, the individual N···O=C interaction energy is about 3.17 kcal mol^{-1}, which is close to the previous *ab initio* calculation (10–13 kJ mol^{-1}).[5] Similar units were also chosen for discussion of the contribution of the C–H···O interaction (in A and B of Fig. 1) to the crystal packing of **1**. The calculated energies of individual C–H···O interactions are about 3.75 kcal mol^{-1} in A and 1.07 kcal mol^{-1} in B. The stabilization energies from C–H···O interaction within the **1·1** dimer (Fig. 1, a) and the branching trimer **1·1·1** (Fig. 1, b) are 7.5 kcal mol^{-1} and 2.41 kcal mol^{-1}, respectively. Comparison of these energies revealed that the N···O interaction should be able to compete with the other two types of C–H···O interactions in the stabilization of crystal packing of **1**.

The ^{1}H NMR spectrum of **1** also shows that the protons of **1** are all electron deficient, which is consistent with the calculated charge distribution. In DMSO-d$_6$, the signals for amide proton and three phenyl ring hydrogens are at δ 11.72, 8.84, 8.63, and 8.43, respectively. In CDCl$_3$, interestingly, the signal for amide proton shifted downfield at δ 12.2 and the three phenyl ring hydrogens shifted downfield from δ 8.6 to 9.2. The maximum shift of the phenyl ring hydrogen is about δ 0.5 (Fig. 3). However, the methyl protons show no shift in both solutions, suggesting that the hydrogens of the phenyl ring all form hydrogen bonds in CDCl$_3$ solution. Dilution studies were conducted in CDCl$_3$ solution in the concentration range of 1–50 mM, but no shift was observed for all the proton resonances. This implies that the protons of the phenyl ring and NH are all involved in forming intramolecular hydrogen bonds in CDCl$_3$ solution. In DMSO-d$_6$, intramolecular hydrogen bonds were broken by competing with the solvent molecules.

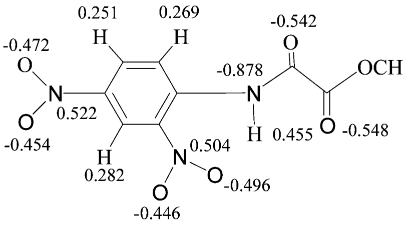

Fig. 2 Charge distribution of **1** (calculated at the HF/6-31G* level).

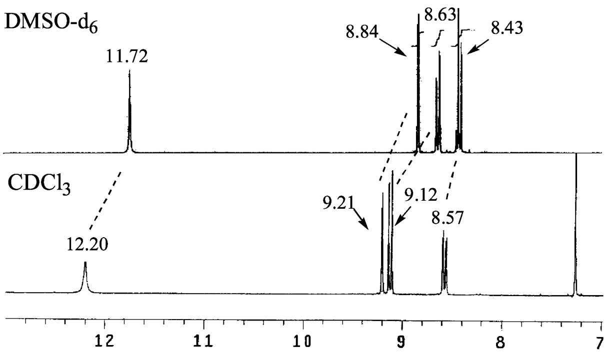

Fig. 3 Part of the ^{1}H NMR spectrum (300 MHz, room temperature) of **1** in DMSO-d$_6$ (top) and in CDCl$_3$ (bottom), clearly showing the downfield shift of the amide proton and phenyl ring hydrogen in CDCl$_3$ solution.

In conclusion, a new type of N···O=C interaction has been found in the crystal packing of compound **1**. This, together with the inter- and intra-molecular C–H···O hydrogen bonds, is demonstrated to be responsible for the self-assembly of **1** in the solid state. On the basis of crystal analysis and *ab initio* calculations, it is confirmed that the formation of an N···O=C interaction is mainly attributed to electrostatic interactions.

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Notes and references

‡ *Crystal data* for **1**: $C_9H_7N_3O_7$, M = 269.18, T = 293(2) K, monoclinic, space group $P2(1)/c$, a = 12.810(3), b = 4.645(2), c = 18.340(5) Å, α = 90, β = 99.330(10), γ = 90°, V = 1076.8(6) Å^3, Z = 4, ρ = 1.660 mg cm^{-3}, μ = 0.146 mm^{-1}, 4643 reflections collected, 2145 unique [R_{int} = 0.0822], final R indices [$I > 2\sigma(I)$]: $R1$ = 0.0496, $wR2$ = 0.0634, R indices(all data): $R1$ = 0.2132, $wR2$ = 0.0883. CCDC 211978. See http://www.rsc.org/suppdata/cc/b3/b306012h/ for crystallographic data in CIF or other electronic format.

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