organic compounds

3-Nitrophenol–4,4′-bipyridyl N,N′-dioxide (2/1): a DFT study and CSD analysis of DPNO molecular complexes

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The title 2:1 complex of 3-nitrophenol (MNP) and 4,4′-bipyridyl N,N′-dioxide (DPNO), $2C_6H_5NO_3 \cdot C_{10}H_8N_2O_2$ or 2MNP·DPNO, crystallizes as a centrosymmetric three-component adduct with a dihedral angle of 59.40 (8)° between the planes of the benzene rings of MNP and DPNO (the DPNO moiety lies across a crystallographic inversion centre located at the mid-point of the C—C bond linking its aromatic rings). The complex owes its formation to O—H···O hydrogen bonds [O···O = 2.605 (3) Å]. Molecules are linked by intermolecular C—H···O and C—H···N interactions forming $R_2^1(6)$ and $R_2^2(10)$ rings, and $R_6^6(34)$ and $R_4^4(26)$ macro-rings, all of which are aligned along the [$\bar{1}$01] direction, and $R_2^2(10)$ and $R_2^1(7)$ rings aligned along the [010] direction. The combination of chains of rings along the [$\bar{1}$01] and [010] directions generates the three-dimensional structure. A total of 27 systems containing the DNPO molecule and forming molecular complexes of an organic nature were analysed and compared with the structural characteristics of the dioxide reported here. The N—O distance [1.325 (2) Å] depends not only on the interactions involving the O atom at the N—O group, but also on the structural ordering and additional three-dimensional interactions in the crystal structure. A density functional theory (DFT) optimized structure at the B3LYP/6-311G(d,p) level is compared with the molecular structure in the solid state.

Comment

The title compound, 2MNP·DPNO (MNP is 3-nitrophenol and DPNO is 4,4′-bipyridyl N,N′-dioxide), (I), belongs to a series of molecular systems based on DNPO with diverse hydrogen-bond donors (Moreno-Fuquen et al., 2003; Lou & Huang, 2007). Crystal engineering with desired functions and unexpected topological architectures is of great interest in the area of solid-state science (Fujita et al., 1995; Hagrman et al., 1999). Much effort has focused on supramolecular network analysis with noncovalent interactions. This interest is motivated by the role played by hydrogen bonds and other weak interactions in molecular recognition (Aruksankunwong et al., 2006) and on the physical, chemical and biological properties of crystal systems (Steiner & Saenger, 1995; Zhang et al., 2008). In this work, we have chosen the 4,4′-bipyridine N,N′-dioxide and 3-nitrophenol adduct (DPNO·MNP), considering its potential for participating in hydrogen bonding. To complement this analysis, 27 different organic crystalline systems, where the DPNO is involved in the formation of supramolecular networks, have been compared [Cambridge Structural Database (CSD), Version 5.29; Allen, 2002]. It is of interest to analyse the behaviour of DPNO in these different crystal environments and examine which structural parameters are affected by the formation of molecular complexes.

(I)
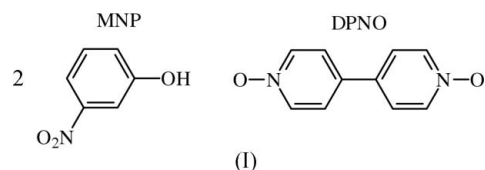
A perspective view of (I), showing the atom-numbering scheme, is given in Fig. 1. This 2MNP·DPNO molecular complex owes its formation to an intermolecular hydrogen bond between the O—H group of the MNP molecule and the N—O group of the DPNO molecule, with an O3···O4 distance of 2.605 (3) Å (Fig. 1). The dihedral angle between the planes of the MNP and DPNO rings is 59.40 (8)°. The distances and bond angles of (I) [N2—O4 = 1.325 (2) Å, C7—N2—O4 = 119.8 (2)° and C11—N2—O4 = 120.1 (2)°] are similar to those found in free DPNO (Thaimattan et al., 1998) and MNP (Wojcik et al., 2006; Hamzaoui et al., 2007).

The analysis of 27 different organic molecular systems where DPNO is involved allows us to examine the behaviour and structural affinities of this molecule. A detailed analysis of the behaviour of the DPNO adduct shows three parameters that are affected by the formation of molecular complexes with different H-atom donors, namely the N—O bond length, the interplanar angle between the rings and the C—C bond length between the rings.

For the title structure, an N—O bond distance of 1.325 (2) Å, a coplanar arrangement between the rings of the DPNO molecule and a C9—C9^v distance of 1.496 (4) Å are observed [symmetry code: (v) −x, −y + 1, −z + 2]. The title structure shows a dihedral angle between the DPNO and MNP molecules of 59.40 (8)°. In the various structures involving DPNO, the O atom of the N—O group is involved in the formation of several intermolecular interactions, including hydrogen bonding. The oxide O is linked to hydrogen-bond
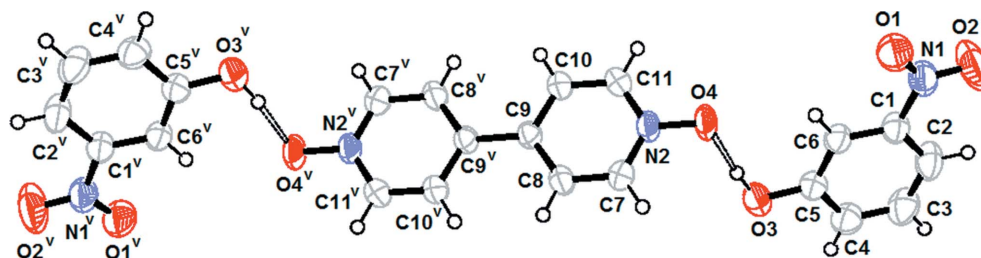
Figure 1
The molecular structure of the components of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. [Symmetry code: (v) $-x$, $-y + 1$, $-z + 2$.]

donors, forming O···H—O, O···H—N and weak O···H—C interactions. The change in the N—O bond length was examined in 78 structures of pyridine N-oxide complexes, and a mean value of 1.293 Å in free N-oxide groups was reported (Eichhorn, 1987). Among these N-oxide systems, such as 4-nitropyridine N-oxide, the N—O bond is shorter than the mean value, at 1.260 Å (Eichhorn, 1956). In the series of 27 organic compounds with DPNO, shorter N—O bond lengths [1.296 (4) and 1.297 (3) Å] are observed in the structure of 9,9′-biacridine N,N'-dioxide (CSD refcode GINSAY; Liu, 2007). In this system, the molecular building blocks are based on bulky acridine N-oxide rings with a T-shaped conformation (torsion angles between the planes of the rings are close to 80°). This indicates steric hindrance between the H atoms of adjacent benzene rings, affecting the ability of the N—O group to form multiple hydrogen-bond interactions and thus inhibiting further elongation of the N—O bond. Even so, this structural feature allows the formation of supramolecular chains of $R_2^2(18)$ rings (Etter, 1990) along the [$\bar{2}$01] direction by weak N···H—C interactions.

The longest N—O bond in this CSD analysis is observed in 4,4′-bipyridinium cis,cis-cyclohexane-1,3,5-tricarboxylic acid 4,4′-dipyridine-N,N'-dioxide cyclohexane-1-carboxylate-cis,cis-3,5-dicarboxylic acid dihydrate (CSD refcode JAWWUA; Bhogala $et\ al.$, 2005), where the DPNO molecule is part of an unusual system, a ternary cocrystal. The O atom of the N—O group in the DPNO molecule is positioned in different environments in the formation of hydrogen bonds. In the first N—O group, the O atom forms hydrogen bonds with two different donor molecules: with the cis,cis-cyclohexane-1,3,5-tricarboxylic acid molecule (CTA) in the bc plane [O···O = 2.6306 (16) Å] and with a water molecule in the ab plane

[O···H—O = 2.7949 (18) Å]. These interactions affect the N—O bond length [1.338 (2) Å]. In the second N—O group, the O atom is linked to one molecule of CTA only [O···H—O = 2.5605 (18) Å], resulting in a shorter N—O bond [1.321 (2) Å]. The O···H—O hydrogen-bond angles are more or less similar in these interactions (∼168°).

The difference in the N—O bond lengths in these structures depends not only on the interactions formed by the O atom of the N—O group, but also on the structural ordering and additional three-dimensional interactions in the crystal structure. In the case of JAWWUA (Bhogala $et\ al.$, 2005), for the first N—O group, the formation of chains of large rings with an $R_8^8(50)$ motif in the bc plane allows the interaction of DPNO, CTA, water and pyridine molecules with each other. In some sections of this chain, the presence of local charges is observed. For the second N—O group, molecules of DPNO, CTA and water form $R_6^6(42)$ rings in the ab plane, but these molecules are distant from one another and have no additional interactions between them.

In this series, symmetric lengthening of the N—O bonds of DPNO is also observed in some compounds where there is coplanarity between the rings of the DPNO molecule [CSD refcodes VIGGEY (Babu $et\ al.$, 2007), OCOMUO (Messina $et\ al.$, 2001), MEGDIM (Reddy $et\ al.$, 2006), LICJUD (Lou & Huang, 2007), LAPLEU (Zeng $et\ al.$, 2005) and HUZCUA (Moreno-Fuquen $et\ al.$, 2003)]. Thus, in analysing the behaviour of supramolecular systems that exhibit this property, we can conclude that the environments formed by the hydrogen bonds at both N—O groups of the DPNO molecule are identical. An inversion centre in these compounds confirms this behaviour. Additionally, a dependency between the C9—C9^v and N—O bond lengths is observed [symmetry code: (v)
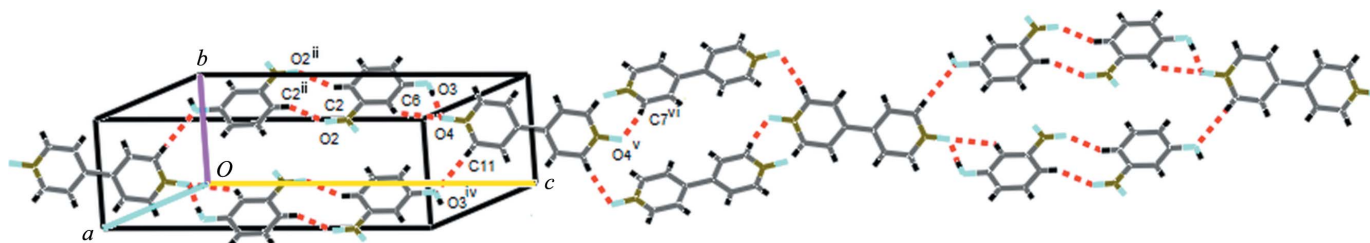
Figure 2
Part of the crystal structure of (I), showing the formation of $R_2^1(6)$ and $R_2^2(10)$ rings, and $R_6^6(34)$ and $R_4^4(26)$ macro-rings running along the [$\bar{1}$01] direction. [Symmetry codes: (ii) $-x + 1$, $-y + 2$, $-z + 1$; (iv) x, $y - 1$, z; (v) $-x$, $-y + 1$, $-z + 2$; (vi) x, $-y + \frac{3}{2}$, $z + \frac{1}{2}$.]
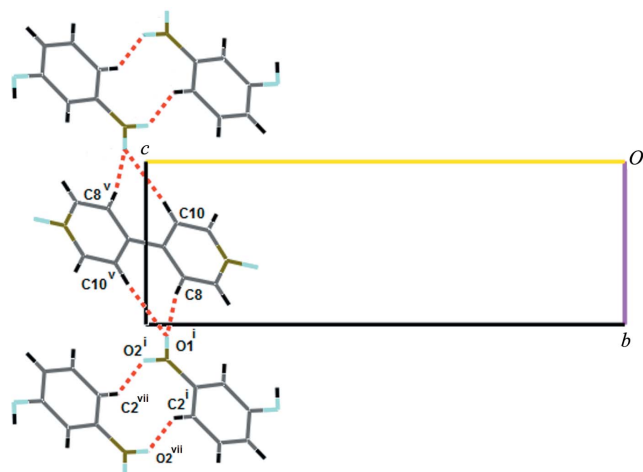
Figure 3
Part of the crystal structure of (I), showing the formation of $R_2^2(10)$ and $R_2^1(7)$ rings running parallel to the [210] direction. [Symmetry codes: (i) $-x, y + \frac{1}{2}, -z + \frac{3}{2}$; (v) $-x, -y + 1, -z + 2$; (vii) $x - 1, -y + \frac{5}{2}, z + \frac{1}{2}$.]

$-x, -y + 1, -z + 2$]. The shorter N—O bond length, the greater C9—C9^v distance (CSD refcodes BAFTEH and BAFVEJ; Thaimattam *et al.*, 1998). This effect becomes evident when the dihedral angle between the DPNO rings increases (CSD refcode GINSAY; Liu, 2007).

We next undertook a theoretical study of the adduct. The crystallographic structure parameters of (I) were used as a starting point for the calculations. The density functional theory (DFT) method was applied, with the B3LYP hybrid exchange correlation function (Becke, 1993; Lee *et al.*, 1988) and the 6-311G(d,p) basis set (Bauschlicher & Partridge, 1995), as implemented in *GAUSSIAN03* (Frisch *et al.*, 2004). The results are presented in Tables S1 and S2 in the *Supplementary Material*, together with experimental data obtained by X-ray diffraction.

The optimized geometry shows differences with respect to the experimental crystal structure for the N2—C7 and N2—C11 bond lengths (see Table S1). The C9—C9($-x$, $-y + 1$, $-z + 2$) distance is very close between the two structures. The theoretical study also gives a dihedral angle of 30.32° between the planes of the DPNO and MNP rings and different values for the N2—O4 bond lengths (1.2939 and 1.2655 Å) [experimental values: 59.40 (8)° and 1.325 (2) Å]. The reason for the discrepancy between the observed and calculated values should be considered in terms of the effects of crystal packing.

The experimental structure of (I) shows O—H⋯O hydrogen-bonding interactions, and also exhibits weak C—H⋯O and C—H⋯N intermolecular interactions (see Table 1) (Nardelli, 1995). The molecules of the adduct are linked into a two-dimensional substructure built from O—H⋯O and C—H⋯N hydrogen bonds and weak C—H⋯O interactions, generating a continuous framework structure. The construction of the first substructure is obtained from the cooperation of five different hydrogen bonds and weak interactions that bind to a DPNO molecule. The formation

chains of different rings is observed between DPNO molecules along the [$\bar{1}$01] direction (Fig. 2). Indeed, for the formation of the first type of ring, interactions between DPNO and MNP molecules are observed. For this, atom O3 in the molecule at (x, y, z) acts simultaneously as a hydrogen-bond donor to atoms O4 in the molecule at (x, y, z). In turn, atom C6 in the molecule at (x, y, z) acts as hydrogen-bond donor to atom O4 in the molecule at (x, y, z), and atom C2 in the molecule at (x, y, z) acts as hydrogen-bond donor to atom O2 in the molecule at ($-x + 1$, $-y + 2$, $-z + 1$). These interactions allow the formation of $R_2^1(6)$ and $R_2^2(10)$ rings. An additional interaction, in which atom C11 in the molecule at (x, y, z) acts as hydrogen-bond donor to atom O3 in the molecule at (x, $y - 1$, z), allows the formation of a large ring with an $R_6^6(34)$ motif, which includes the previous rings. The formation of the second type of ring is based only on the interactions between the DPNO molecules. Thus, atom C7 in the molecule at (x, $-y + \frac{3}{2}$, $z + \frac{1}{2}$) acts as hydrogen-bond donor to atom O4 in the molecule at ($-x$, $-y + 1$, $-z + 2$), so generating by translation an $R_4^4(26)$ centrosymmetric ring (Fig. 2). In the second one-dimensional substructure within the asymmetric unit of (I), atom C8 in the molecule at (x, y, z) and atom C10 in the molecule at ($-x$, $-y + 1$, $-z + 2$) act as hydrogen-bond donors to atom O1 in the molecule at ($-x$, $y + \frac{1}{2}$, $-z + \frac{3}{2}$), so forming an $R_2^1(7)$ ring. At the same time, atom C2 at ($-x$, $y + \frac{1}{2}$, $-z + \frac{3}{2}$) acts as hydrogen-bond donor to atom O2 at ($x - 1$, $-y + \frac{5}{2}$, $z + \frac{1}{2}$), thus forming an $R_2^2(10)$ ring. Both rings run along the [210] direction (Fig. 3). The combination of these chains of rings along [$\bar{1}$01] and [010] is sufficient to generate the three-dimensional structure of (I).

In summary, this crystallographic study has allowed the analysis of 27 systems containing the DPNO molecule that form molecular complexes of an organic nature. The N—O bond distance [1.325 (2) Å] depends on the angle between the planes of the DPNO rings. A tendency for symmetric stretching of the N—O bond lengths is observed when the rings of the DPNO molecule are coplanar. It is also noted that, as the angle between the planes of the DPNO molecule increases, the N—O bond length decreases.

A DFT calculation on (I) identified a structure with a dihedral angle of 30.32° between the planes of the MNP and DPNO rings. This situation revealed the presence of two different N—O distances. There is a modest relationship with a decrease in the N—O bond length that leads to an increase in the C9—C9($-x$, $-y + 1$, $-z + 2$) distance. This behaviour is represented effectively in the GINSAY complex (Liu, 2007), and repeated in most of the systems analysed. The N—O distance depends not only on the interactions formed by the O atom at the N—O group, but also on the structural ordering and additional three-dimensional interactions in the crystal structure.

Experimental

Reagents and solvents for the synthesis were purchased from Aldrich and were used without additional purification. Pale-yellow single crystals of the title molecular complex, (I), suitable for X-ray analysis were obtained by slow evaporation of an equimolar solution of MNP

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and DPNO in acetonitrile. The crystals of the MNP–DPNO complex have a melting point of 589 (1) K.

Crystal data

$2C_6H_5NO_3 \cdot C_{10}H_8N_2O_2$
$M_r = 466.4$
Monoclinic, $P2_1/c$
$a = 10.5167$ (14) Å
$b = 5.9729$ (13) Å
$c = 18.2602$ (10) Å
$\beta = 105.700$ (7)°

$V = 1104.2$ (3) Å^3
$Z = 2$
Mo $K\alpha$ radiation
$\mu = 0.11$ mm^{-1}
$T = 291$ K
$0.32 \times 0.19 \times 0.15$ mm

Data collection

Rigaku AFC-7S diffractometer
2052 measured reflections
1937 independent reflections
1243 reflections with $I > 2\sigma(I)$

$R_{int} = 0.016$
2 standard reflections every 150 min
  intensity decay: none

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.048$
$wR(F^2) = 0.130$
$S = 1.01$
1939 reflections
158 parameters

H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max} = 0.13$ e Å^{-3}
$\Delta\rho_{min} = -0.21$ e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O3—H31$\cdots$O4	0.96 (3)	1.65 (3)	2.605 (3)	175 (3)
O3—H31$\cdots$N2	0.96 (3)	2.44 (3)	3.329 (3)	154 (2)
C8—H8$\cdots$O1^i	0.93	2.37	3.290 (3)	170
C7—H7$\cdots$O4^i	0.93	2.36	3.278 (3)	168
C2—H2$\cdots$O2^{ii}	0.93	2.48	3.295 (3)	146
C6—H6$\cdots$O4	0.93	2.54	3.196 (3)	128
C10—H10$\cdots$O1^{iii}	0.93	2.50	3.428 (3)	172
C11—H11$\cdots$O3^{iv}	0.93	2.51	3.397 (3)	161

Symmetry codes: (i) $-x, y + \frac{1}{2}, -z + \frac{3}{2}$; (ii) $-x + 1, -y + 2, -z + 1$; (iii) $x, -y + \frac{1}{2}, z + \frac{1}{2}$; (iv) $x, y - 1, z$.

Atom H31 was located in a difference map and its coordinates were refined freely. All other H atoms were located in difference maps and then treated as riding atoms, with C—H = 0.93 Å and $U_{iso}(H) = 1.2U_{eq}(C)$.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1993); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *Mercury* (Macrae *et al.*, 2008); software used to prepare material for publication: *PARST95* (Nardelli, 1995).

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