

A Competition Between N---O and C---O Through Space Interactions in the Crystal Structures of 3,3'-Dinitro-2,2'-bipyridine N-Oxides and N,N'-Dioxides.

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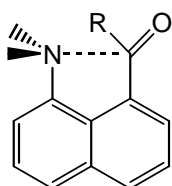
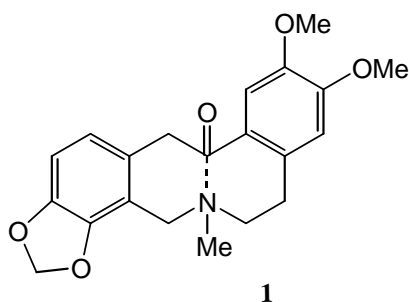
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Abstract.

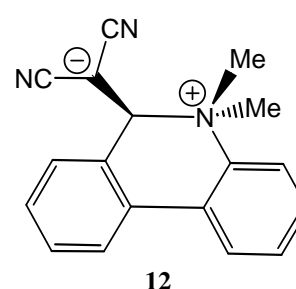
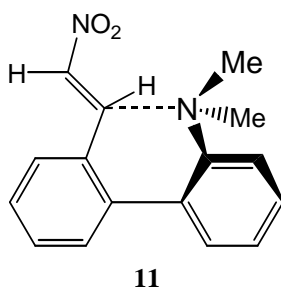
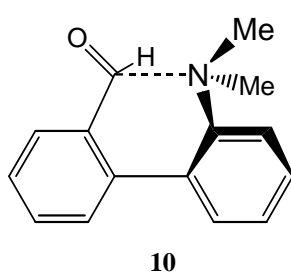
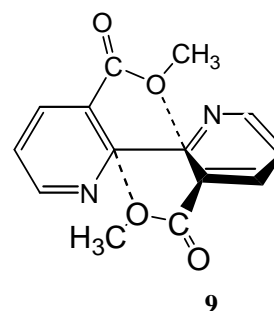
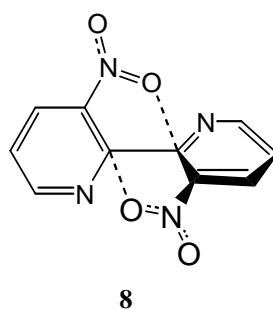
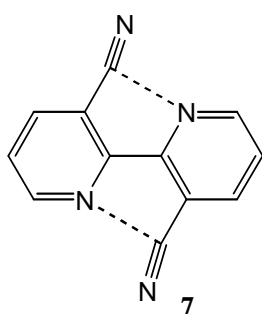
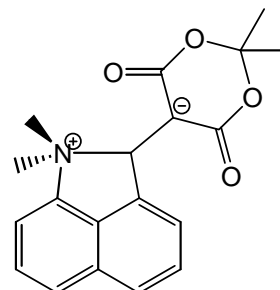
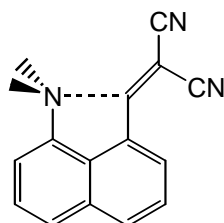
The crystal structures of a series of 3,3'-dinitro-2,2'-bipyridine N-oxides and N,N'-dioxides consistently show 1,5 interactions between nitro oxygen atoms and aromatic carbon atoms ((ON)O---C: 2.623(2)-2.839(2) Å) while there are also 1,6 interactions between N-oxide oxygen atoms and nitro nitrogen atoms in most cases (O---N(O₂): 2.737(2)-2.874(3) Å). The O---C interactions appears to be a common feature in *ortho*-nitro-biphenyl systems, and there is some evidence that the effect is cooperative when there are *ortho* nitro groups on both rings. The O---N interactions are considerably longer than the corresponding 1,5 N---O interaction measured here in 8-nitroquinoline-1-oxide (O---N(O₂): 2.5418(17) Å), which in turn is longer than the corresponding N---O interaction in the corresponding 8-diazonium-1-oxide analogue.

Introduction.

Interactions between an electron-rich and an electron-poor group have been studied by X-ray crystallography over a number of years, following the initial work of Bürgi and Dunitz on the interactions between amino groups and carbonyl compounds in compounds such as **1**.¹ Pairs of groups located at the *peri* positions of a naphthalene ring have provided an important system for studying the effects of two groups held in close proximity,² and an order of reactivity for electrophilic sp^2 carbon centres has been constructed³ from interaction distances with a dimethylamino group as in **2-5**.^{2,4-5} In the latter series a bond was almost completely formed between these groups in a few cases, e.g. in **6**,^{3,6} and a related zwitterionic structure in the azaadamantane series has been reported.⁷ The reactivity of a methylthio group as a nucleophilic centre has also been studied,⁸ as have interactions with sp C centres in nitriles⁹ and alkynes.¹⁰ Anthracene systems have been used in a similar way for studying functional group interactions.¹¹ Further insight into these *peri*-interactions is being gained by studies of the topology of the electron density in the region between the groups.¹² A few 3,3'-disubstituted 2,2'-bipyridines have also been studied, since the ring nitrogen provides a nucleophilic centre. Thus, a pair of interactions was observed in the dinitrile **7** with (pyridine)N--C \equiv N separations of 2.695(2) and 2.740(2) Å, and bendings of the nitrile groups of 171.3(1)-171.6(1)°. ¹³ However, extension of this approach to groups with sp^2 centres attached to the 3 and 3' positions, e.g. in compounds **8** and **9** containing nitro or carboxylic ester groups, did not reveal such interactions between the pyridine nitrogen and the electron deficient group, but rather an oxygen atom from each group made a contact with the 2-carbon atom of the opposite ring (**8**: 2.916(2) and 2.980(2) Å; **9**: 2.849(3) Å).^{14,15} These

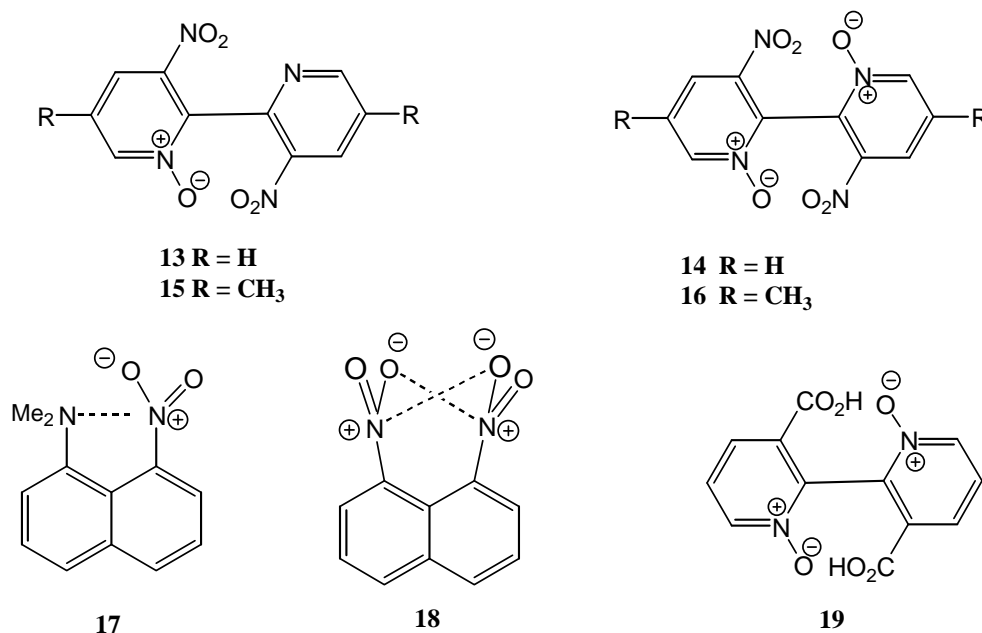


- 2** R = CH₃
3 R = H
4 R = NMe₂



peri-naphthalene and bipyridine frameworks provide 1,5 interactions between the functional groups. In contrast, positioning the substituents in the *ortho* positions of a biphenyl allows the groups to form 1,6 interactions in which they can approach each other without concomitant strain, but also there is sufficient freedom for the groups to rotate well out of interaction range too. Thus, dimethylamino groups form long contacts, more like intermolecular interactions, with sp²C centres in an aldehyde or a 2-nitroethene in **10** and **11**, but form a bond with more reactive groups such as 2,2-

dicyanoethene as in **12**.¹⁶ Here, we report structural studies on the N-oxides and N,N'-dioxides of 3,3'-dinitro-2,2'-bipyridine and their 5,5'-dimethyl derivatives, **13-16**, to explore whether the oxide group acts as a nucleophilic centre and is involved in 1,6 contacts with the nitrogen atom of a nitro group, or whether the tendency for a nitro oxygen to make 1,5 interactions with the opposite ring system still prevails. The nitrogen atoms of nitro groups have been observed to make interactions with electron rich centres such as dimethylamino groups and nitro oxygen atoms before, as in the *peri*-naphthalenes **17**¹⁷ (N---N: 2.64-2.72 Å) and **18** (O----N: 2.682-2.722 Å).¹⁸



Results and Discussion

3,3'-Dinitro-2,2'-bipyridine and its 5,5'-dimethyl derivative were each oxidized with 3-chloroperbenzoic acid in chloroform at 34-50°C to give mixtures of their N-oxide and N,N'-dioxide, which were separated by chromatography on basic alumina to give **13-16**. Crystals of each compound were prepared by slow evaporation. X-ray diffraction data were collected at 150 K (**13** and **14**) and 120 K

(**15** and **16**). The molecular structures are shown in Figures 1-4. Selected molecular geometric data are given in Table 1, along with data for the N,N'-dioxide of bipyridine-3,3'-dicarboxylic acid **19**¹⁹ for which the structure has been reported on both its racemate and on a single enantiomer. There are no other structures measured for 3,3'-disubstituted 2,2'-bipyridine N-oxides or -dioxides.

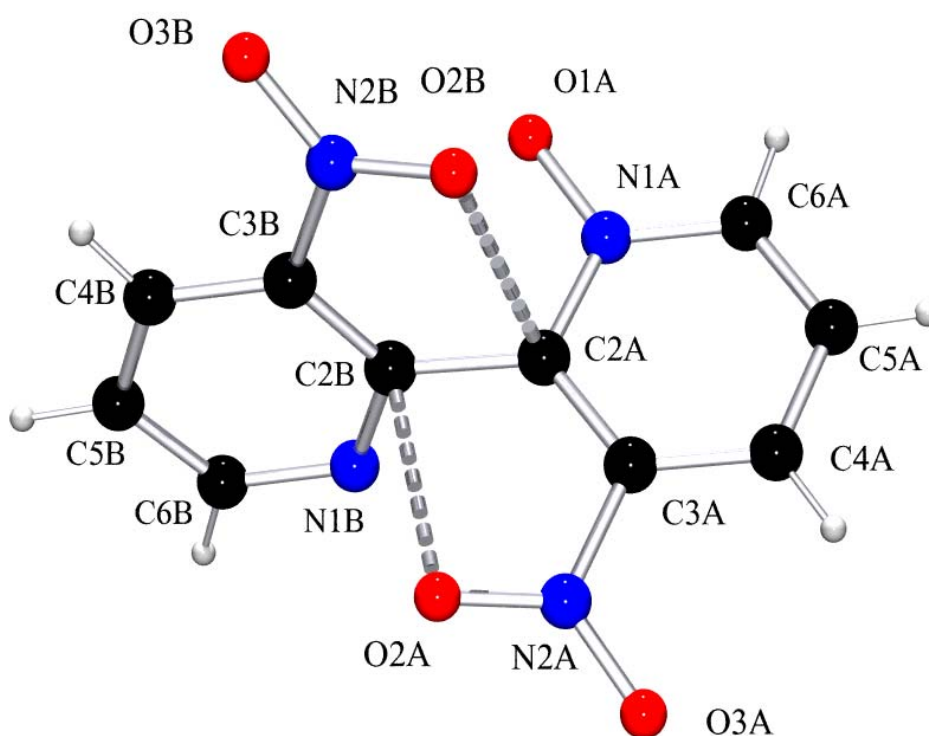


Figure 1. Molecular structure of N-oxide **13**; the O...N separation between oxide oxygen and nitro nitrogen is more than 3 Å.

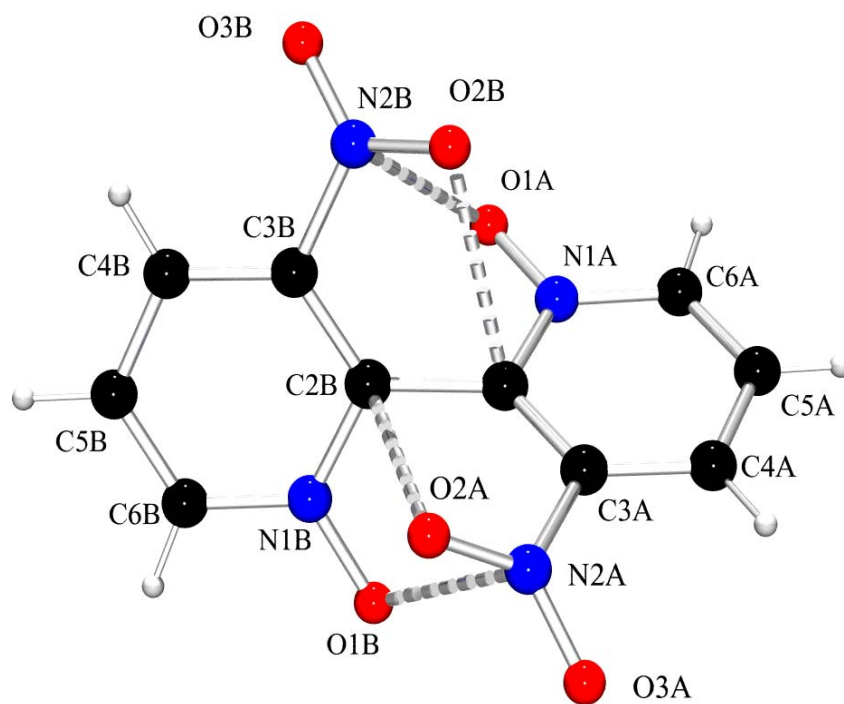


Figure 2. Molecular structure of dioxide **14**.

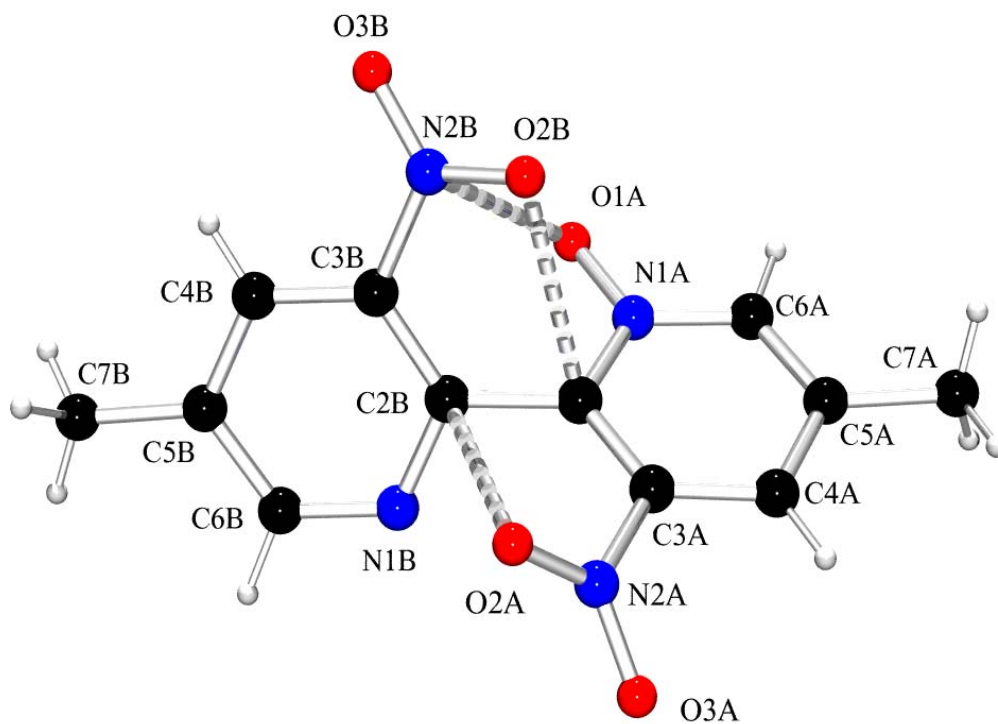


Figure 3. Molecular structure of dimethyl substituted N-oxide **15**.

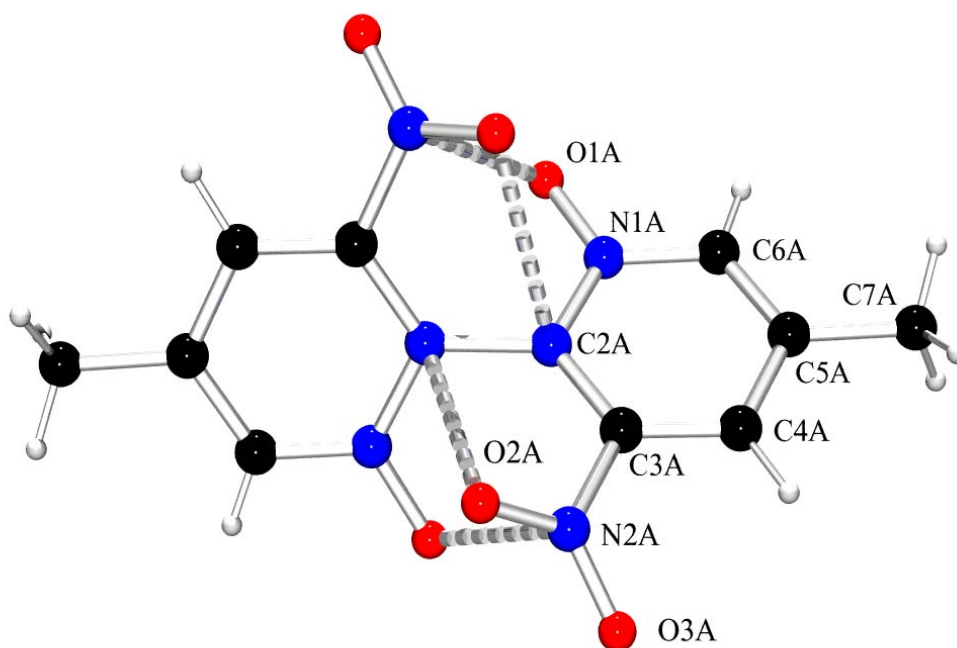
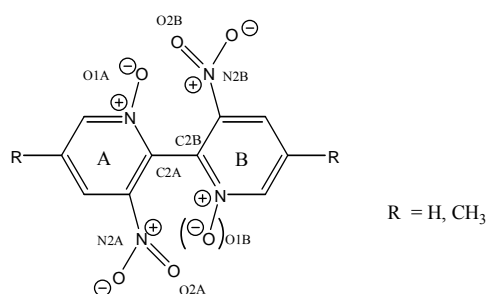


Figure 4. Molecular structure of dimethyl-substituted N,N'-dioxide **16**;
the two halves of the molecule are related by a crystallographic 2_1 axis.

The two dioxides, **14** and **16**, show similar molecular conformations with the pyridine rings lying at 52.8 - 55.8° to each other, and the nitro groups lying at 33.3 - 36.9° to their respective pyridine rings, so that each N-oxide oxygen atom lies at $2.737(3)$ - $2.804(3)$ Å from a nitro nitrogen atom of the opposite ring. Furthermore, an oxygen atom from each nitro group lies at $2.762(4)$ - $2.789(3)$ Å from the carbon atom (C2) of the opposite ring at the end of the inter-ring bond. Compared to the unoxidized dinitroipyridine **8**, this corresponds to an increase in the inter-ring angle of *ca.* 10° caused by presence of the two additional N-oxide oxygen atoms, while each nitro group's plane deviates less from their pyridine ring's plane to maintain and shorten the contact to the carbon atom of the opposite ring.

Table 1. Selected Geometric Data for Compounds **13-16** and Related Molecules (\AA , $^\circ$)

	O2A--C2B	O2B--C2A	O1A---N2B	O1B--N2A	Angle ring (A) / ring (B) from trans coplanar / $^\circ$	Angle ring (A) / NO ₂ (A) / $^\circ$	Angle ring (B) / NO ₂ (B) / $^\circ$
	/ \AA	/ \AA	/ \AA	/ \AA			
8 ¹⁴	2.916(2)	2.980(2)	*	*	42.9(1)	42.8(1)	52.0(1)
13	2.644(2)	2.623(2)	3.140(2)	*	72.22(5)	18.2(2)	19.8(2)
14	2.772(3)	2.762(4)	2.771(6)	2.804(3)	55.8(1)	35.3(3)	33.3(3)
15 ^a	2.839(2)	2.726(2)	2.874(3)	*	55.9(1)	40.9(1)	22.8(2)
16 ^b	2.789(3)	*	2.737(3)	*	52.84(5)	36.9(2)	*
	O2A--C2B	O2B--C2A	O1A-- C(O ₂ H)	O1B-- C(O ₂ H)	Angle ring (A) / ring (B)	Angle ring (A) / CO ₂ H (A)	Angle ring (B) / CO ₂ H (B)
Rac- 19 ¹⁹	2.748(9)	*	3.055(9)	*	68.1(2)	22.8(2)	*
Ent- 19 ¹⁹	2.757(5)	*	3.159(5)	*	71.4(2)	23.0(2)	*
	2.749(5)	*	4.027(5)	*	105.6(2)	16.6(2)	*

^a 8% Disorder in the location of the oxide oxygen atom.

^b Only half of **16** is crystallographically unique.

There is no such consistency in the structures of the unsymmetrical oxides, **13** and **15**. Structure **15** is broadly similar to those of **14** and **16**. The pyridine rings lie at 55.9° so that the O---N separation between the adjacent N-oxide atom and nitro nitrogen atom remains close to those in **14-16** since the inter-ring rotation is the main factor controlling this separation. The two nitro groups lie at 41° and 23° to their respective ring planes, the latter being the nitro group near to the N-oxide group. Since the O---C separation between a nitro oxygen and the opposite ring's C2 carbon atom is controlled primarily by the angle of rotation of the nitro group out of its plane, with lower angles of rotation corresponding to closer contacts, there are now two distinct O---C separations, one longer ($2.839(2)$ Å) and one shorter ($2.726(2)$ Å) than those observed in the dioxides. In contrast, in the structure of N-oxide **13** there is a much larger angle between the pyridine ring planes ($72.22(5)^\circ$), so that the separation between the N-oxide oxygen atom and the nitro nitrogen atom is extended to $3.140(2)$ Å i.e. essentially out of van der Waals contact. However, the two nitro groups lie at only $18.2(2)$ and $19.8(2)^\circ$ out of their respective pyridine planes, leading to the closest 1,5 contacts between nitro oxygen atoms and ring C2 carbon atoms in this series at $2.644(2)$ and $2.623(2)$ Å. Thus, the two sets of potential interactions have similar separations in each of compounds **14-16**, but in the monoxide **13** the interaction between nitro oxygen and ring carbon is much shorter than between the N-oxide oxygen and nitro nitrogen atom. The analogous dicarboxylic acid N,N'-dioxide **19** has been measured in both its racemic and enantiopure form.¹⁹ Of the three crystallographically unique molecules, two have broadly similar conformations to the N-oxide **13**, with contacts between a N-oxide oxygen atom and a carbonyl carbon of $3.055(9)$ Å and $3.159(5)$ Å. The third molecule has its pyridine rings at 74.4° from the *cis* coplanar conformation, and thus a considerably longer separation between the N-

oxide oxygen atom and the carbonyl carbon of 4.027(5) Å. In all three molecules, there are short 1,5 interactions between the carbonyl oxygen atoms (2.748(9) – 2.757(5) Å) and the carbon at the far end of the inter-ring bond. Thus, as for the dinitro oxides and dioxides **13-16** 1,6 interactions of N-oxide oxygen atoms with the 3-substituents do not dominate the structures, but interactions between a nitro oxygen and a ring carbon are always present. In all four dinitro compounds **13-16**, most oxygen atoms also make intermolecular interactions with ring hydrogen atoms, and in the diacid **19** hydrogen bonding necessarily plays an important role in determining the crystal packing.

Table 2. Orientations of Approach of the N-Oxide Oxygen Atom to the Nitro Group.

	O1'---N2-O2/ ^o	O1'---N2-O3/ ^o	O1'---N2-C3/ ^o
13	77.20(9)	119.04(11)	73.86(8)
14	86.7(2)	103.6(2)	80.23(19)
	89.7(2)	104.2(3)	77.9(2)
15	82.68(12)	112.08(14)	75.73(11)
16	87.35(12)	102.40(12)	81.66(11)

Table 3. Orientations of Approach of the Nitro Oxygen Atom O2' to the Ring Carbon C2

	O2'---C2-N1/ $^{\circ}$	O2'---C2-C3/ $^{\circ}$	O2'---C2-C2/ $^{\circ}$
13	87.08(9)	106.7(11)	79.27(9)
	88.64(9)	103.69(11)	77.78(9)
14	81.27(17)	111.7(2)	76.61(18)
	81.65(19)	113.6(3)	76.18(19)
15	81.99(12)	116.45(12)	76.83(11)
	84.23(12)	113.56(13)	74.20(11)
16	78.98(12)	114.72(15)	75.90(12)

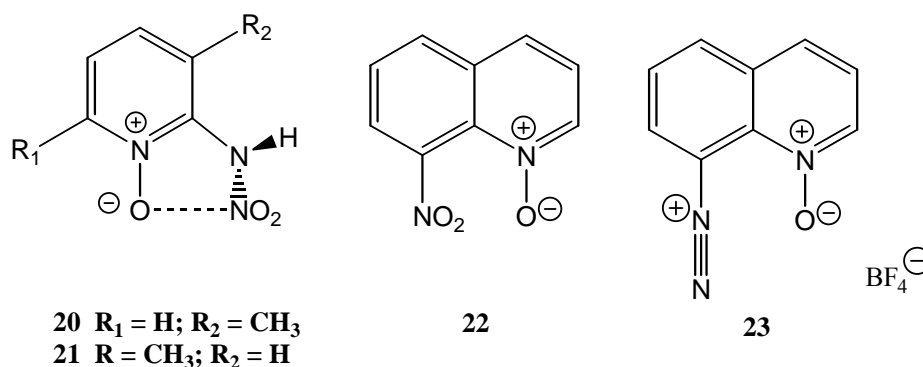
The orientations of the approach of (a) the N-oxide oxygen atom to the nitro group and (b) of the nitro oxygen atom to the pyridine carbon atom are controlled by both the angular displacements of the pyridine rings and their nitro groups. The geometries of these approaches is given in Tables 2 and 3. Thus, the (N)-O---N(O₂) vector lies in the range 73.86-81.66 $^{\circ}$ to the bond from the nitro group to carbon, and in the ranges 77.20-89.74 $^{\circ}$ and 102.40-119.04 $^{\circ}$ to the nitro N-O₂ and N-O₃ bonds respectively. The only *intramolecular* contacts between pyridine-N-oxide oxygen atoms and nitro nitrogen atoms recorded in the Cambridge Structural Database²⁰ are in **20** and **21** where these (1,5) separations are 2.864(2) and 2.872(2) Å,²¹ though these nitramino groups will be more electron rich than standard nitro groups and thus not

Table 4. Details of Hydrogen Bonding Interactions Between Oxygen Atoms and Ring Hydrogen Atoms in **13**, **15-16**.

H---O	H---O/Å	Angle O---H-C /°
Molecule 13		
H(4A) O(2B) [1/2 - X , 1/2 + Y , 1 - Z]	2.425(18)	146.5(14)
H(4B) O(2A) [1/2 - X, Y - 1/2, - Z]	2.352(18)	165.2(14)
H(5A) O(3B) [1/2 - X , 1/2 + Y , 1 - Z]	2.65(2)	143.9(16)
H(5B) O(1A) [- X , - Y , - Z]	2.527(18)	132.3(13)
H(6A) O(1A) [- X , - Y , 1 - Z]	2.298(16)	173.1(14)
H(6B) O(3A) [- X , 1 - Y , -Z]	2.605(16)	131.7(13)
Molecule 15		
H(4A) O(1A) [1/2 - X , 1/2 + Y , 1 - Z]	2.34(2)	148.5(16)
H(4B) O(2A) [- X , - Y , - Z]	2.69(2)	138.1(17)
H(6A) N(1B) [- X , - Y , 1 - Z]	2.89(2)	116.8(17)
H(6B) O(2B) [-1 +X, Y , Z]	2.66(2)	138.3(15)
H(6B) O(3A) [+ X -1/2 , 1/2 - Y , Z]	2.54(2)	128.2(16)
H(7A1) O(3B) [1/2 - X , 1/2 + Y , 1 - Z]	2.75	145
H(7A2) O(1A) [1/2 - X , 1/2 + Y , 1 - Z]	2.38	142
H(7A3) O(2B) [1 - X , - Y , 1 - Z]	2.66	133
H(7B2) O(3B) [-1/2 + X , -1/2 - Y , Z]	2.42	151
H(7B3) O(2A) [- X , - Y , - Z]	2.69	128
H(7B3) O(2B) [[- X , - Y , - Z]	2.56	131
Molecule 16		
H4A O1A [-1/2 + X , -1/2 + Y , Z]	2.27(3)	150(2)
H6A O1A [- X , - Y , 1 - Z]	2.72(3)	128(2)
H6A O3A [X , - Y , - 1/2 + Z]	2.88(3)	137(2)
H72 O2A [-1/2 + X , -1/2 - Y , -1/2 + Z]	2.45	128
H73 O3A [X , - Y , - 1/2 + Z]	2.42	145

as good at accepting electron density through space. The shortest twenty intermolecular contacts between N-oxide oxygen atoms and the nitrogen atoms of standard nitro groups reported lie in the higher range 2.918-3.089 Å.²⁰ Thus, most of

our N-O---NO₂ interactions are shorter than any of these, and 2.737(2) Å in **16** is the shortest. Later we describe the structure of 8-nitroquinoline-N-oxide **22**, in which these two groups are forced to lie *peri* to one another, and show an even shorter N---O contact of 2.5418(17) Å. The shortest intramolecular O---N=O contacts between nitro groups recorded in the Cambridge Structural Database are considerably shorter than the intramolecular (N)O---NO₂ contacts we observe in structures **13-16**. Thus there are over 100 examples of such contacts in the range 2.525-2.699 Å ($R < 0.06$, $\sigma(\text{C-C}) < 0.01$ Å). Although an oxide group is a much better nucleophile than a nitro group's oxygen atom, the electrons in the nitro group are drawn in more, so that the effective size of its oxygen atoms is reduced.



For comparison with the O---C contacts observed in **13-16**, we have surveyed the role of *ortho* nitro or carboxyl groups on the conformations of biphenyls in the solid state, to see whether 1,5 contacts between oxygen atoms and carbon atoms of the opposite benzene ring are observed.²⁰ There is not so much data published. The five biphenyls carrying an *ortho* nitro group on each ring and no other *ortho* substituents have inter-ring angles of 62-137° including one perpendicular arrangement.²² In all cases there are 1,5 O---C contacts of the type observed in our pyridine series, in the range 2.701-2.875 Å, with the shorter contacts corresponding

to those cases where the nitro group lies less out of the benzene plane. Steric interaction of a nitro group with the opposite *ortho* substituent (H or NO₂) does not appear to be the controlling feature, since the minimum (O₂)N---H contacts are *ca.* 3.0 Å and the minimum (O₂)N---O(NO) contacts are *ca.* 2.87 Å. For 2,2'-dinitrobiphenyl itself the rings lie at 62.5°, with nitro group planes at 56.5° from their pyridine rings, O---C contacts are 2.810(2) Å and the (O₂)N---H contacts are 3.0 Å. There are twelve biphenyls carrying just one nitro group as the only *ortho* substituent which show inter-ring angles in the range 46-133° and each shows a (1,5) O---C contact between a nitro oxygen atom and the carbon at the end of the inter-ring bond in the range 2.839-3.108 Å.²³ The higher range for this contact distance over the dinitro cases, suggests that there may be an element of cooperativity in the disubstituted cases, i.e. both carbons at the end of the inter-ring bond are depleted of electron density by a through-bond interaction with the nearer nitro group, and thus make a more effective through-space interaction with the other nitro group. The one example of a biphenyl with four *ortho* nitro groups, **24**, measured by Read et al.,²⁴ is a particularly instructive case. This molecule carries two (*meta*) amino groups and three nitro groups on each ring. The benzene rings lie at 83.8°, and the two *ortho* nitro groups whose planes lie closest to their benzene ring planes (6.7° and 39.3°) make very short (1,5) O---C contacts of 2.472(5) and 2.487(6) Å respectively (Fig 5). Bond lengths suggest charge delocalisation from the amino groups into the nitro groups. Thus, these nitro groups are more electron rich, yet at the same time the *ortho* nitro groups also remove electron density from the ring carbon atom involved in the interaction, both factors which should make the interaction more significant than in the dinitro biphenyls. There are notable exocyclic distortions at the benzene rings at the inter-ring bond, such that the inter-ring bond is splayed away from each of the

two interacting nitro groups. These are the shortest intramolecular (ON)O---C(phenyl) contacts known.

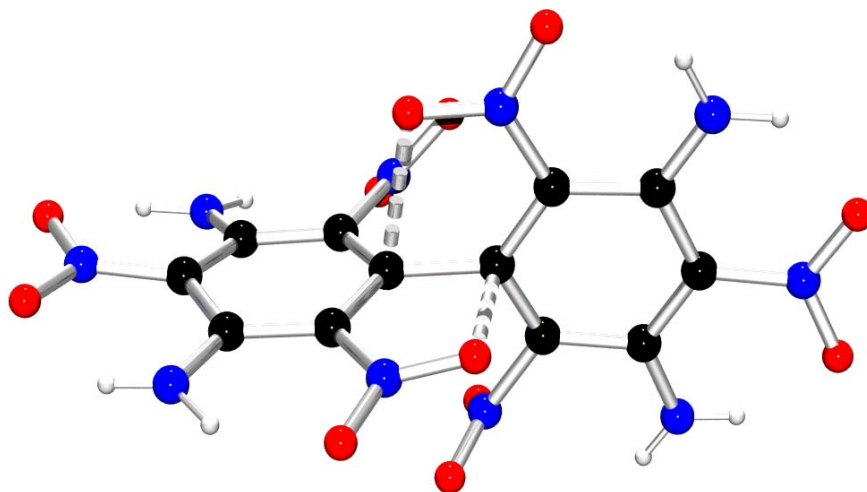
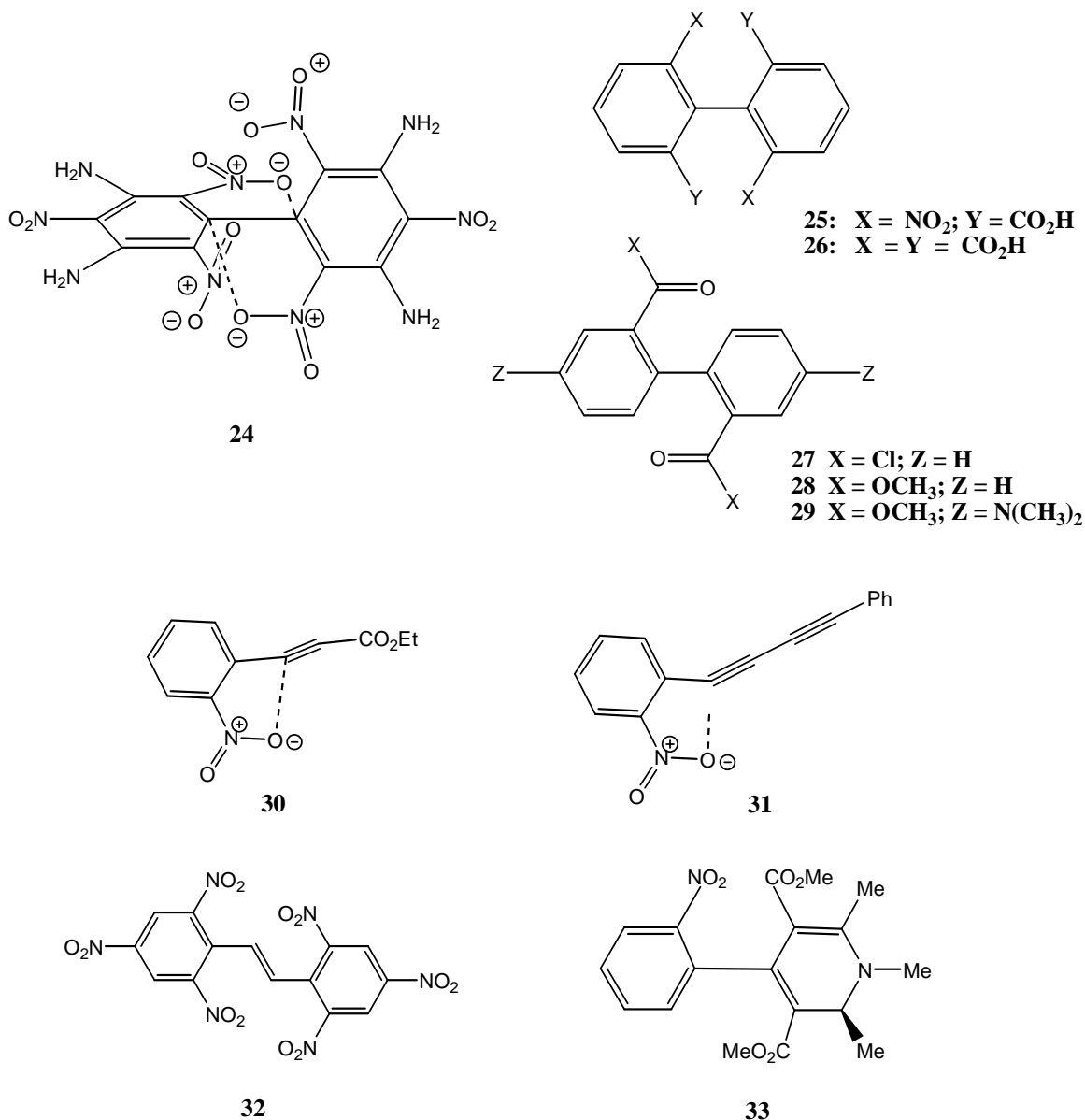


Figure 5. Molecular structure of **24** measured by Read et al.²⁴ showing the two short O---C interactions $< 2.5 \text{ \AA}$

Examination of the eight biphenyls²⁵ carrying four *ortho* substituents from the set of nitro, carboxylic acid and carboxylic ester shows that they make four short 1,5 O...C contacts (range: 2.599-3.054 \AA with a mean value of 2.766 \AA) pinning the biphenyl into a conformation with roughly perpendicular phenyl rings (78-90°). This includes the structure of the 2,2'-dinitrobiphenyl-6,6'-dicarboxylic acid **25**²⁶ and the tetracarboxylic acid **26**.²⁷ Biphenyl-2,2'-dicarboxylic acids also show 1,5 O---C interactions in the range 2.726-3.031 \AA (mean 2.867 \AA),²⁸ and biphenyl-2,2'-



dicarbonyl chloride **27**²⁹ and the two dimethyl biphenyl-2,2'-carboxylate derivatives **28-29**³⁰ also show the corresponding C=O...C contacts (**27**: 2.741 Å, **28-29**: 2.807-2.903 Å). Nitro groups also known to make short contacts with alkynes and dialkynes e.g. in **30** and **31** (2.636(2) - 2.642(2) Å),³¹ and to alkenes (2.617-2.791 Å for eight particularly short ones)³² such as **32** and **33**.

Crystal Structures of 13-16.

Oxide **13** contains the shortest O---C contact due to the smallest displacements of the nitro groups from their pyridine planes. The two types of N,O bond are well differentiated, with the N-O oxide bond length of 1.3023(16) Å and the much shorter nitro N,O bond lengths in the range 1.2181(17)-1.2293(17) Å. The geometry at the two ring nitrogens are distinctly different: the endocyclic angle at nitrogen is 120.87(13)° at the oxidized nitrogen atom, but 117.62(12)° at the unoxidized nitrogen atom, and the ring bond lengths to the oxidized N atom are longer by 0.02-0.03 Å (N1A,C2A 1.3677(19) cf. N1B,C2B 1.3353(18) Å and N1A,C6A 1.3592(19) cf. N1B,C6B 1.339(2) Å). In the crystal structure (Fig. 6) molecules are linked in pairs by two optimal hydrogen bonds (2.298(16) Å) between N-oxide oxygen atoms and hydrogen atoms *ortho* to the ring nitrogen atom (Fig. 7). Each nitro oxygen atom make one intermolecular hydrogen bond (2.35-2.65 Å) (Table 4), the shorter hydrogen bonds involving the more electron deficient H4 (*ortho* to nitro) and H6 (*ortho* to the ring nitrogen atom).

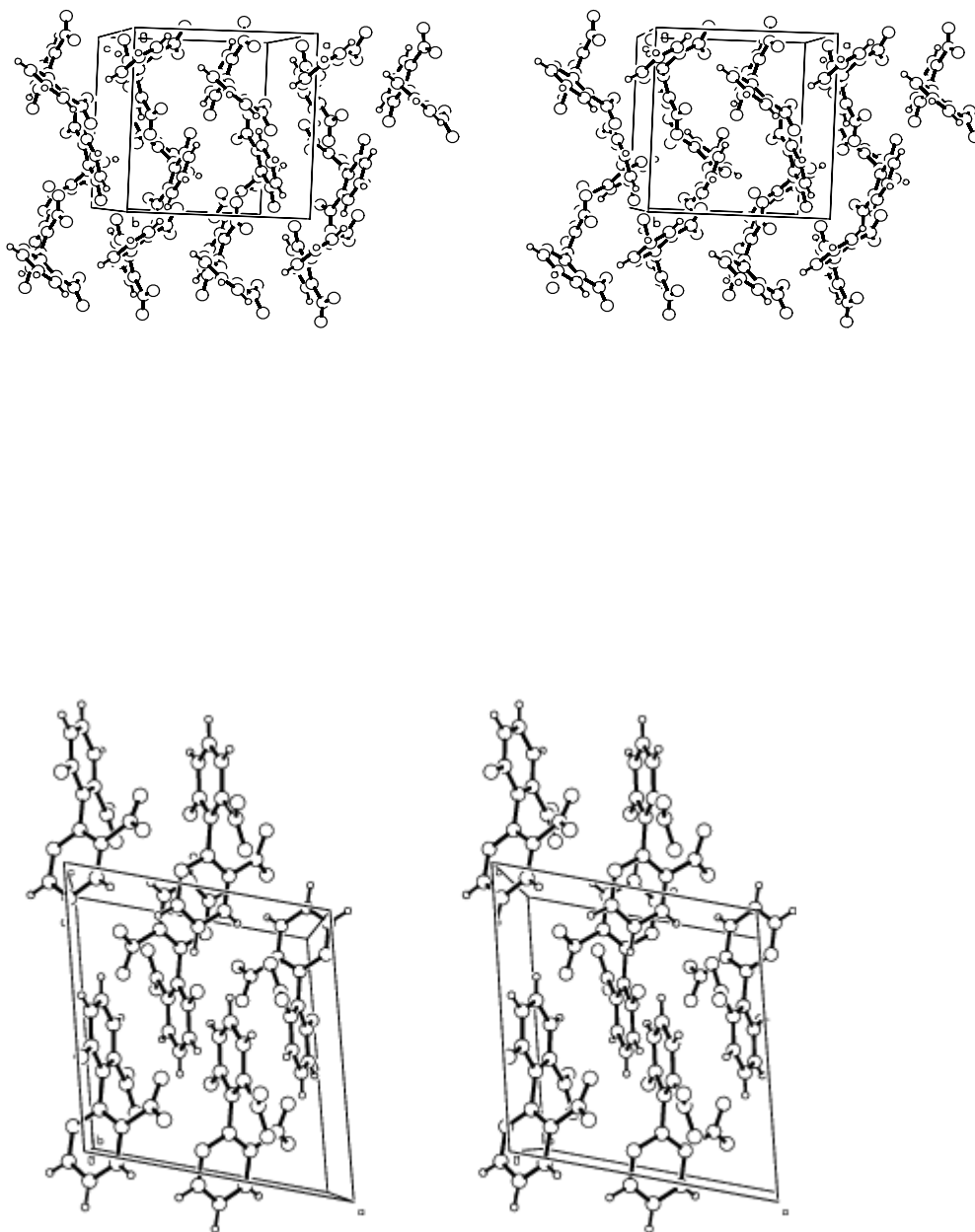


Figure 6. Stereo crystal packing diagram for **13** viewed down the *b* axis.

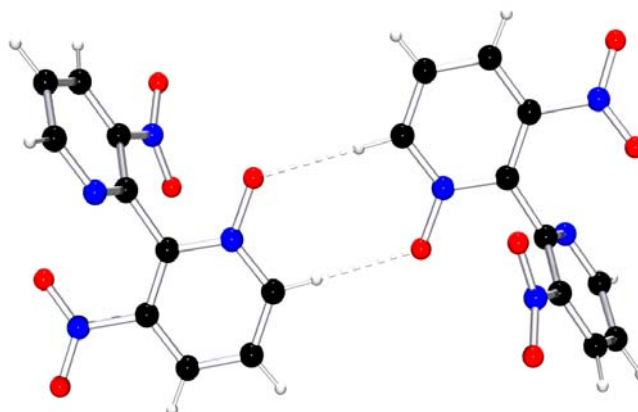


Figure 7: Linking of molecules of **13** in pairs with hydrogen bonds.

The low temperature structure of dioxide **14** could be refined to an R factor of 5.7% using a triclinic cell of dimensions $6.1226 \times 7.4847 \times 13.5200 \text{ \AA}^3$, $\alpha = 102.8525$, $\beta = 90.226$, $\gamma = 111.154^\circ$, but the ellipsoids were systematically, moderately elongated in one direction. However, some extra diffraction spots were observed in the diffraction pattern of **14** and they can be indexed to a very large cell of dimensions $20.3578 \times 22.7139 \times 22.7139 \text{ \AA}^3$, $\alpha = 89.5742$, $\beta = 87.1617$, $\gamma = 74.5216^\circ$. We have not been able to make a full analysis of this superstructure. Thus, we note the geometry of the structure refined from the smaller cell, but it should not be interpreted too deeply. Nevertheless, the overall conformation of this structural solution is broadly similar to that of the dimethylated dioxide **16**.

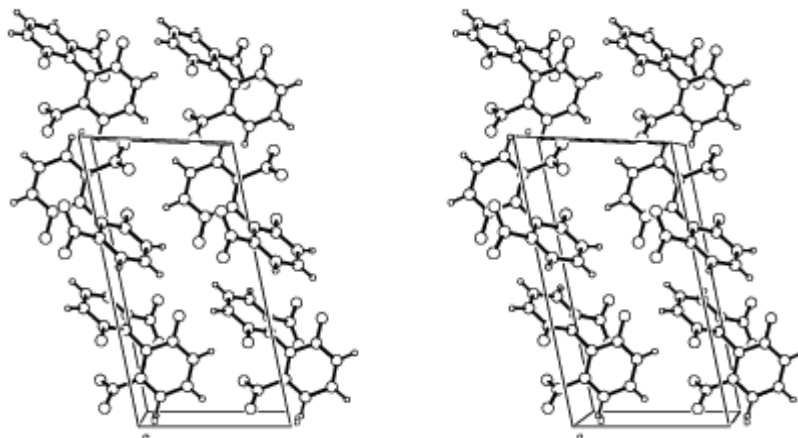


Figure 8. Stereo crystal packing diagram of **14** based on the triclinic cell.

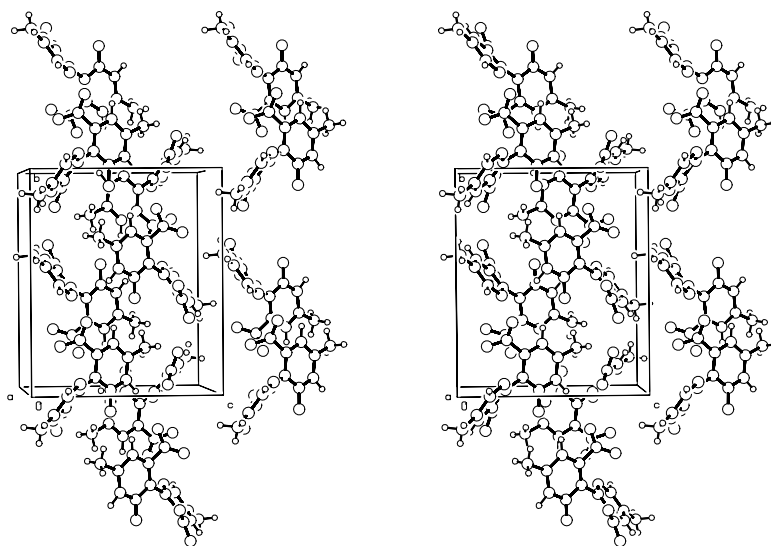


Figure 9. Stereo crystal packing diagram of **15**.

In the crystal structure of the dimethyl disubstituted oxide **15** there is a 92:8 disorder in the location of the N-oxide oxygen atom on the two possible pyridine ring sites. The crystal packing diagram (Fig. 9) is constructed with the major component only, but there is sufficient space around the unoxidized pyridine nitrogen atom to

accommodate the alternatively located oxygen atom with only a small disturbance to the lattice. The molecules are linked together by hydrogen bonding between N-oxide oxygen atoms and hydrogen atoms *ortho* to nitro groups (2.30(2) Å) and the neighbouring methyl group.

The dimethylated dioxide **16** lies on a crystallographic twofold axis so that only one half of the molecule is crystallographically unique. The N-oxide N,O bond length is 1.302(2) Å and the nitro N,O bond lengths 1.221(2) and 1.221(2) Å. The molecules are assembled into layers in the *ab* plane by O1---H4 hydrogen bonds (2.27(3) Å). The methyl groups project from each face of the layer, and adjacent layers interlock with the methyl groups lying close to nitro groups of the next layer (O---H, 2.42-2.45 Å) (Fig. 10). It is notable that molecules **13-16** all have high densities, 1.55-1.65 g cm⁻³, because of the efficiency possible in packing compact molecular structures.

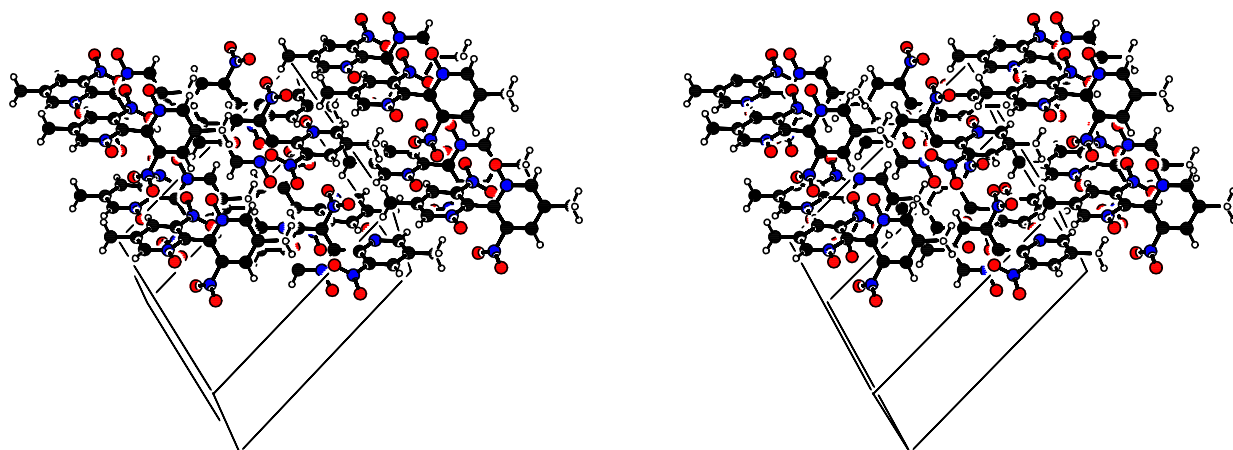


Figure 10. Stereo crystal packing diagram for **16** viewed down the *b* axis.

Crystal Structure of 8-Nitroquinoline-N-oxide.

The O---N interactions between N-oxide oxygens and nitro nitrogen atoms in structures **13-16** are 1,6 interactions, but the groups are not forced to be near one another. In contrast, if the groups are oriented *peri* to each other on a polycyclic aromatic system, then the groups are forced to be near one another at a separation of *ca.* 2.5 Å and the attractive or repulsive nature of the interaction between the groups

at this sort of separation can be estimated from the displacements of the groups towards or away from each other. To provide a comparison with this type of interaction in **13-16**, we have determined the structure of 8-nitroquinoline-N-oxide **22**,³³ in which the two groups are located *peri* to each other. The molecule is shown in Fig. 11 and its crystal packing arrangement in Fig. 12. The nitro group lies almost perpendicular to the quinoline plane and the N-O...NO₂ separation is 2.5418(17) Å, much shorter than observed in oxide and dioxides **13-16**, though of course in this compound the groups have less opportunity to escape each other. Nevertheless, the nitro group is only displaced away from the oxide oxygen atom by about 3° (the exocyclic angles at the quinoline ring differ by 6.3°), while the oxide oxygen atom is displaced slightly towards the nitro group (difference in exocyclic ring angles 1.7°). The O---N interaction vector makes angles of 95.41° and 95.96° with the nitro N,O bonds. The oxide oxygen atom and nitro nitrogen atoms lie very close to the quinoline plane from which they are very slightly displaced by 0.067(1) and 0.089(1) Å in opposite directions. The nitro group is slightly pyramidalised, and the nitrogen atom displaced by 0.036(1) Å towards the oxide oxygen atom. This is a larger deviation from planarity than observed for any of the nitro groups in bipyridine derivatives **13-16**. The molecules are packed in stacks along the *a* axis with adjacent molecules related by a centre of symmetry, while the stacks are related by two fold screw axes. There is one particularly short intermolecular contact between the hydrogen atom *ortho* to the ring nitrogen, H2, and a nitro oxygen atom (O3) (2.30 Å) from a molecule in a neighbouring stack. This hydrogen bond has an angle of 164.9(13)° at the H atom and 117.7(4)° at the oxygen atom. The only other structure of a 8-substituted quinoline-N-oxide reported is for the diazonium analogue **23** in which the O---N distance is 2.443(2) Å.³⁴ This, at least, indicates that the diazonium

group is a better through space acceptor of electron density than the nitro group. Nucleophilic attack at the α -nitrogen of a diazonium group leads only to a high energy 1,1-diazene intermediate, but this interaction only corresponds to a very early stage of such a process. Glaser³⁵ has proposed that short contact of oxygen with the α -nitrogen of a diazonium is better described as a 1,3 bridging interactions of the oxygen centre with the two atoms attached to the α -nitrogen. The shortest N---N contacts between dimethylamino and nitro groups in the corresponding *peri*-substituted naphthalene are longer (2.64-2.67 Å) than the N---O contact in this quinoline N-oxide.¹⁷

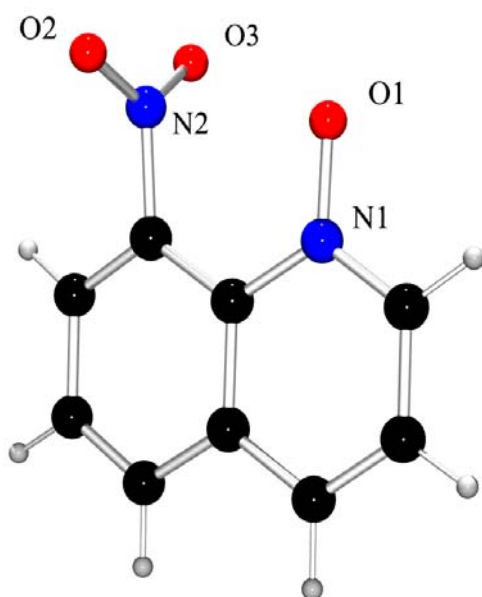


Figure 11. Molecular structure of 8-nitroquinoline-N-oxide **22**.

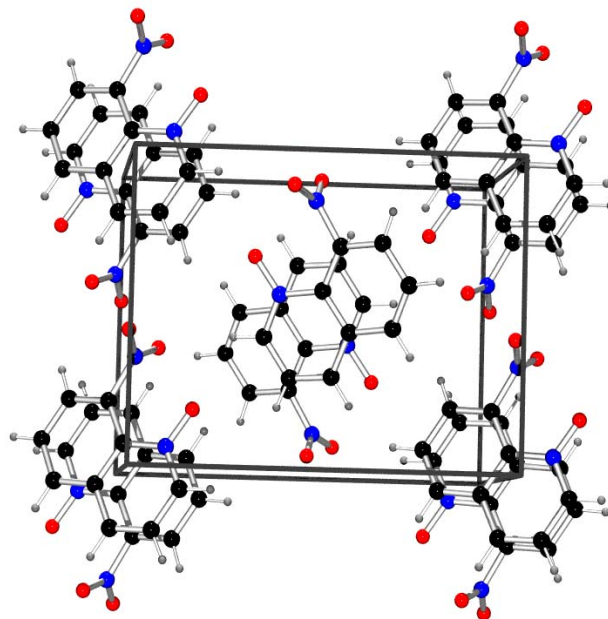


Figure 12: Crystal packing of **22** viewed down the *a* axis.

In summary, although *peri*-naphthalene **22** shows a short 1,5 O---NO₂ contact, the corresponding 1,6 interactions in the bipyridine oxides and dioxides **13-16** face competition from 1,5 O---C interactions. In **13-16** none of the interactions are forced by the connectivity of the molecules. There is evidence from the Cambridge Structural Database, that the latter interaction may play a significant role in control of conformations of biphenyls carrying several nitro groups in *ortho* positions. While the N---O interactions may involve a very small degree of covalent interaction, the O---C interactions are likely to be electrostatic and enhanced by polarisation of the π aromatic cloud by the nitro oxygen atoms. Future charge density measurements may provide a better understanding of these short contacts.

Experimental

General. NMR spectra were measured on a JEOL JNM-EX270 spectrometer at 270 MHz for ^1H and at 67.8 MHz for ^{13}C and measured in p.p.m. downfield from TMS, unless otherwise stated. IR spectra were recorded on a PerkinElmer Spectrum RX 1 FT-IR spectrometer in cm^{-1} . Mass spectra were recorded at the EPSRC National Mass Spectrometry Centre at Swansea University. X-Ray diffraction datasets were measured by the EPSRC National Crystallography Service at Southampton University.

Preparation of 3,3'-Dinitro-2,2'-bipyridine-1-oxide **13** and 3,3'-Dinitro-2,2'-bipyridine-1,1'-dioxide **14**.

3-Chloroperbenzoic acid (5.98g, 58-84% purity, Aldrich) dissolved in chloroform (60 ml) was added to a solution of 3,3'-dinitro-2,2'-bipyridine **1**³⁶ (2.0 g, 8.12 mmol) in chloroform (140 ml) at 0°C and stirred for 3 h., then stirred at 34°C overnight. Tlc (CHCl_3 with 5% CH_3OH) indicated formation of the monoxide as the main product. More 3-chloroperbenzoic acid (1.70 g) in chloroform (25 ml) was added and the mixture stirred at 50°C overnight. The mixture was poured on to a basic alumina column and subjected to gradient elution (chloroform/methanol, methanol 0-10%) to give the monoxide **2** (0.77 g, 36%) and the dioxide **3** (1.23 g, 54%) as separate fractions.

3,3'-Dinitro-2,2'-bipyridine-1-oxide **13**: m.p. 184-188°C; ^1H NMR (DMSO-d_6) δ : 9.03 (1H, dd, $J = 4.7, 1.2$ Hz, 6'-*H*), 8.81 (1H, dd, $J = 8.4, 1.2$ Hz, 4'-*H*), 8.76 (1H, dd, $J = 6.4, 0.7$ Hz, 6-*H*), 8.28 (1H, dd, $J = 8.6, 0.7$ Hz, 4-*H*), 7.97-7.85 (2H, m, 5,5'-*H*); ^{13}C NMR (DMSO-d_6) δ : 154.3 (6'-*C*), 147.0 & 145.5 (3-,3'-*C*), 143.4 & 142.7 (2-,2'-*C*), 142.0 (6-*C*), 133.2 (4'-*C*), 126.9 & 126.4 (5-,5'-*C*), 122.2 (4-*C*); $\nu_{\text{max}}/\text{cm}^{-1}$: 1600, 1526, 1262, 1028, 864, 824, 815, 766, 738 cm^{-1} ; HRMS (EI): Found: 262.0338, $\text{C}_{10}\text{H}_6\text{N}_4\text{O}_5$ requires: 262.0338.

3,3'-Dinitro-2,2'-bipyridine-1,1'-dioxide 14: m.p. 202-206°C; ^1H NMR (DMSO- d_6) δ : 8.82 (2H, dd, $J = 6.6, 0.7$ Hz, 6-,6'- H), 8.32 (2H, dd, $J = 8.5, 0.7$ Hz, 4-,4'- H), 7.92 (2H, dd, $J = 8.5, 6.6$ Hz, 5-,5'- H); ^{13}C NMR (67.8 MHz, (DMSO- d_6) δ : 147.1 (3-,3'- C), 144.0 (6-,6'- C), 135.5 (2-,2'- C), 127.6 (5-,5'- C), 121.8 (4-,4'- C); $\nu_{\text{max}}/\text{cm}^{-1}$ (nujol): 1555, 1536, 1419, 1278, 1258, 1020, 804, 726; HRMS (EI): Found: 278.0287, $\text{C}_{10}\text{H}_6\text{N}_4\text{O}_6$ requires: 278.0287.

Preparation of 5,5'-Dimethyl-3,3'-dinitro-2,2'-bipyridine-1-oxide 15 and 5,5'-Dimethyl-3,3'-dinitro-2,2'-bipyridine-1,1'-dioxide 16

3-Chloroperbenzoic acid (1.75 g, 10 mmol) was slowly added to a solution of 5,5'-dimethyl-3,3'-dinitro-2,2'-bipyridine³⁷ (0.84 g, 3 mmol) in CHCl_3 (30 ml) at 0°C. The mixture was allowed to warm to room temperature then heated to 50°C for 3 h. before being left to stir at room temperature for 48 h. The mixture was poured on to a basic alumina column and subjected to gradient elution (chloroform/methanol, methanol 0-10%) to give the monoxide **15** (0.09 g, 10%) and the dioxide **16** (0.16 g, 17%).

5,5'-Dimethyl-3,3'-dinitro-2,2'-bipyridine-1-oxide 15: m.p. 211-214°C dec.; ^1H NMR (DMSO- d_6) δ : 8.82 (1H, s, 6'- H), 8.64 (1H, s, 4'- H), 8.60 (1H, s, 6- H), 8.13 (1H, s, 4- H), 2.51 (3H, s, CH_3), 2.43 (3H, s, CH_3); ^{13}C NMR (DMSO- d_6) δ : 154.3 (6'- C), 146.6 & 145.3 (3-, 3'- C), 142.7 (6- C), 139.8 & 139.4 (2-, 2'- C), 137.9 & 137.1 (5-,5'- C), 132.9 (4'- C), 122.9 (4- C), 17.6 & 17.5 (2 x CH_3); $\nu_{\text{max}}/\text{cm}^{-1}$ (KBr): 3035, 2925, 1624, 1542, 1458, 1354, 1289, 1219, 1153, 1027, 863, 780; HRMS (ES): Found: 291.0739 ($\text{M}+\text{H}$)⁺, $\text{C}_{12}\text{H}_{10}\text{N}_4\text{O}_5$ requires: 291.0729 ($\text{M}+\text{H}$)⁺.

5,5'-Dimethyl-3,3'-dinitro-2,2'-bipyridine-1,1'-dioxide 16: m.p. 211°C dec.; ^1H NMR

(DMSO- d_6) δ : 8.72 (2H, s, 6-,6'-H), 8.23 (2H, s, 4-,4'-H), 2.45 (6H, s, 2 x CH₃); ¹³C NMR (DMSO- d_6) δ : 147.3 (3-,3'-C), 144.0 (6-,6'-C), 139.5 (5-,5'-C), 133.4 (2-,2'-C), 124.4 (4-,4'-C), 18.2 (2 x CH₃); $\nu_{\max}/\text{cm}^{-1}$ (KBr): 3051, 1654, 1617, 1549, 1442, 1378, 1260, 1295, 1225, 1159, 1019, 911, 875, 782, 754; HRMS (ES): Found: 307.0682 (M+H)⁺, C₁₂H₁₀N₄O₆ requires: 307.0679 (M+H)⁺.

Crystal Structure Determinations.

X-Ray diffraction data was measured at low temperature with MoK α radiation and solved and refined with the SHELXS and SHELXL computer programs.³⁸ Hydrogen atom positions were located and refined without constraints, with the exception of the methyl groups in **15** and **16**. Illustrations and geometry calculations with ORTEP³⁹ and PLATON.⁴⁰

Crystal data for **13**: C₁₀H₆N₄O₅, M_r = 262.19, monoclinic, a = 9.873(2), b = 10.671(2), c = 10.577(7) Å, β = 104.583(30)°, V = 1078.47 Å³, Z = 4, P2₁/a, T = 150 K, D_c = 1.61 g cm⁻³, μ (MoK α) = 0.13 mm⁻¹, 8399 measured reflections, theta limits 1.99-27.47°, 2430 unique reflections, 1820 with F_o > 4 σ (F_o), R1 = 0.046, wR2 = 0.114, resid. electron density 0.28 & -0.29 e Å⁻³. Crystals from methanol.

Crystal data for **14**: C₁₀H₆N₄O₆, M_r = 278.19, triclinic, a = 6.1226 (3), b = 7.4847(4), c = 13.5200(8) Å, α = 102.8252(2)°, β = 90.226(2)°, γ = 111.154(3)°, V = 560.99 Å³, Z = 2, P $\bar{1}$, T = 150 K, D_c = 1.65 g cm⁻³, μ (MoK α) = 0.14 mm⁻¹, 6412 measured reflections, theta limits 1.55-24.97°, 1916 unique reflections, 1279 with F_o > 4 σ (F_o), R1 = 0.057, wR2 = 0.140, resid. electron density 0.47 & -0.42 e Å⁻³. However, extra diffraction spots are present in the diffraction pattern of **14** and a very large cell of

dimensions 20.3578 x 22.7139 x 22.7139 Å³ $\alpha = 89.5742$, $\beta = 87.1617$, $\gamma = 74.5216$ can be used to index them. Crystals from methanol.

Crystal data for **15**: C₁₂H₁₀N₄O₅, M_r = 290.24, monoclinic, a = 8.1670(3), b = 13.4699(6), c = 11.3597(6) Å, $\beta = 94.750(2)^\circ$, V = 1245.37 Å³, Z = 4, P2₁/a, T = 120 K, D_c = 1.55 g cm⁻³, μ (MoK α) = 0.12 mm⁻¹, 9531 measured reflections, theta limits 2.92-27.49°, 2826 unique reflections, 1949 with F_o > 4 σ (F_o), R1 = 0.055, wR2 = 0.145, resid. electron density 0.38 & -0.35 e Å⁻³. There is a small degree of disorder, in which about 8% of the molecules carry the oxide O atom on the second ring N atom. Only the alternative position of the O atom was included in the final model. Crystals from methanol.

Crystal data for **16**: C₁₂H₁₀N₄O₆, M_r = 306.24, monoclinic, a = 12.044(4), b = 7.544(3), c = 15.093(5) Å, $\beta = 108.480(3)^\circ$, V = 1300.66 Å³, Z = 4, C2/c, T = 120 K, D_c = 1.56 g cm⁻³, μ (MoK α) = 0.13 mm⁻¹, 6827 measured reflections, θ limits 2.85-27.49°, 1462 unique reflections, 1272 with F_o > 4 σ (F_o), R1 = 0.057, wR2 = 0.150, resid. electron density: 0.44 & -0.31 e Å⁻³. Crystals from methanol.

Crystal data for **22**: C₉H₆N₂O₃, M_r = 190.16, monoclinic, a = 7.8557(6), b = 8.8130(6), c = 11.4793(10) Å, $\beta = 93.780(4)^\circ$, V = 793.01 Å³, Z = 4, P2₁/n, T = 120 K, D_c = 1.59 g cm⁻³, μ (MoK α) = 0.12 mm⁻¹, 8940 measured reflections, θ limits 3.83-27.51°, 1809 unique reflections, 1465 with F_o > 4 σ (F_o), R1 = 0.043, wR2 = 0.11, resid. electron density 0.24 & -0.30 e Å⁻³. Crystals from methanol.

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QUJGEH, QUJGIL, SAJJET, SEFYEH

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