# Structural Investigation of 2,6-Di-2-furyl-3,5-dimethyl-4-piperidinone and Its *N*-Nitroso Derivative in Solution and the Solid State-Influence of the Nitroso Moiety on the Conformation of the Piperidine Ring and Orientation of Its Substituents

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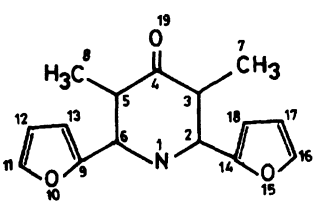
The structures of the title compounds, 2,6-di-2-furyl-3,5-dimethyl-4-piperidinone (DFMP) and its *N*-nitroso derivative (DFMPNO), have been investigated in solution and the solid state by NMR and X-ray methods, respectively. Both of the structures were solved by direct methods of X-ray analysis and were refined to an *R*-factor of 0.059 and 0.057, respectively. The piperidine ring adopts a *chair* conformation in DFMP and a *boat* conformation in DFMPNO. Both of the furan rings are in an equatorial orientation in DFMP, whereas in DFMPNO one ring is in the axial position and the other ring is in the equatorial position. The nitroso group is in the perpendicular orientation in DFMPNO. The angle between the best plane of the piperidine ring and the nitroso group is 142.1(4)°. The interaction between the molecules are van der Waals in nature in both structures.

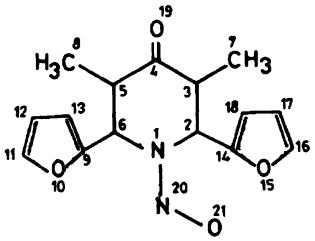
Most nitrosamines are known to be carcinogenic in nature.[1—3] It has also been observed that blocking the position $\alpha$ to the ring nitrogen atom by methyl groups in cyclic nitrosamines reduces the carcinogenic activity.[4] Some of the *N*-nitrosoureas are used as either antitumor agents or antibiotics.[5,6] It is believed that *N*-nitroso compounds are responsible for the initial step in the process of carcinogenesis by alkylating DNA bases at those sites which contain genetic information pertaining to the cancerous state of the cell.[7,8] Almost all of the piperidine precursors prefer to exist in the chair conformation, with a slight twist or distortion of the ring, depending upon the positions and sizes of the substituents.[9] The aim of this study was to determine the conformations of the *N*-nitroso derivatives, since the introduction of a *N*-nitroso group exerts a large influence on these conformations as well as the orientations of the ring substituents.[10] In view of its importance regarding utility, the reactivity and conformational features of *N*-nitroso compounds, spectroscopic and crystallographic studies of 2,6-di-2-furyl-3,5-dimethyl-4-piperidinone (DFMP) ($C_{15}H_{17}NO_3$) and its *N*-nitroso derivative (DFMPNO) ($C_{15}H_{16}O_4N_2$) were carried out (Schemes 1 and 2).

## Experimental

The $^1H$ and $^{13}C$ NMR spectra were recorded on a Bruker 400 MHz instrument in a $CDCl_3$ solution with TMS used as an internal standard.




Scheme 1. (I) DFMP




Scheme 2. (II) DFMPNO

Crystals of DFMP and DFMPNO were grown by slow evaporation from an ethanol solution at room temperature. Well-shaped colorless crystals were chosen for X-ray diffractometeric measurements on a CAD-4 (Enraf–Nonius) four-circle diffractometer using graphite monochromated Cu $K\alpha$ radiation. Accurate cell parameters of both compounds were obtained by least-squares fittings of the $2\theta$ values of 25 centered reflections in the range $8<\theta<25$ for DFMP and 21 reflections in the range $8<\theta<24$ for DFMPNO. The intensities were measured in the $\omega$–$2\theta$ scan mode. Lorentz, polarisation, absorption and extinction corrections were applied to all of the reflections.

Structure solutions were carried out by direct methods for both compounds using SHELX86.[11] A full-matrix least-squares refinement based on $F_o$ was carried out with non-hydrogen atoms anisotropically for both compounds using an SDP package.[12] All of the hydrogen atoms in DFMP and 14 of the 16 hydrogens in DFMPNO were obtained from a $\Delta\rho$ synthesis. All of the hydrogen atoms in DFMP have been refined isotropically, while in DFMPNO hydrogen atoms were not refined since reflections to the parameter ratio were poor. An individual weighting scheme, in which $w=1/\sigma(F^2)$, $\sigma(F^2)=[\sigma^2(I)+0.04I^2]^{1/2}$ based on counting statistics, was used for both compounds. Atomic scattering factors were taken from "International Tables for X-ray Crystallography," (1974).[13] The computer programs used were PARST,[14] PLUTO,[15] and ORTEP.[16] All of the calculations were performed on VAX 11/730 and MicroVAX

Table 1. Crystal Data

| | DFMP | DFMPNO |
|---|---|---|
| Empirical formula | $C_{15}H_{17}NO_3$ | $C_{15}H_{16}O_4N_2$ |
| Molecular weight ($M_r$) | 257.29 | 288.31 |
| Crystal system | Triclinc | Orthorhombic |
| Space group | $P\bar{1}$ | $P2_12_12_1$ |
| $a$/Å | 8.919(1) | 9.334(1) |
| $b$/Å | 11.478(1) | 20.525(2) |
| $c$/Å | 7.100(1) | 7.708(1) |
| $\alpha$/° | 103.83(1) | 90.0 |
| $\beta$/° | 98.32(1) | 90.0 |
| $\gamma$/° | 93.65(1) | 90.0 |
| Volume/Å$^3$ | 694.68 | 1474.30 |
| $Z$ | 2 | 4 |
| $D_{calcd}$/g cm$^{-3}$ | 1.231 | 1.299 |
| $F(000)$ | 276.0 | 608.0 |
| $\mu$/cm$^{-1}$ | 6.671 | 7.521 |
| $\lambda$ (Cu $K\alpha$)/Å | 1.5418 | 1.5418 |
| Max. time spent on each reflection | 45 s | 60 s |
| Standard reflections | (1 5 2), (1 −4 3), (4 1 1) | (−2 −5 −1), (−3 0 1), (0 1 4) |
| Range/deg [$2\theta_{max}$] | 140° | 140° |
| $h$ | 0→10 | 0→11 |
| $k$ | −14→14 | 0→25 |
| $l$ | −8→8 | 0→9 |
| Mode of absorption | PSI scan | PSI scan |
| Variation of transmission factors | 0.972—0.999 (Ave=0.987) | 0.985—0.999 (Ave=0.993) |
| Reflections collected | 2816 | 1661 |
| No. of unique reflections | 2634 | 1543 |
| Reflections observed | 1890 [$I>3\sigma(I)$] | 936 [$I>1.5\sigma(I)$] |
| Extinction coefficient | $8.458\times10^{-6}$ | $2.391\times10^{-6}$ |
| No. of parameters | 237 | 191 |
| Final residuals $R$ | 0.059 | 0.057 |
| $R_w$ | 0.057 | 0.054 |
| $S[\sum w(\Delta F)^2/(N-P)]^{1/2}$ | 0.654 | 0.966 |
| Max. & Min. ($\Delta\rho$) eÅ$^{-3}$ | ±0.357 | ±0.231 |
| Max ($\Delta/\sigma$) | 0.05 | 0.03 |

II computing systems available in the department. Crystal data and details concerning the refinement are given in Table 1.

## Results and Discussion

The $^1$H and $^{13}$C NMR spectra of DFMP show the existence of a rigid chair conformation with the two heteroaryl and methyl groups in equatorial positions. An equatorial orientation of the substituents was inferred from the diaxial coupling value of the protons at the C-2 and C-3 positions as well as the C-5 and C-6 positions ($^3J_{2a,3a}=^3J_{6a,5a}=10.8$ Hz).

In the $^1$H NMR spectrum of the nitrosamine, the doublets at $\delta=5.47$ ($^3J_{2a,3a}=9.3$ Hz) and 6.20 ($^3J_{5a,6a}=3.3$ Hz) correspond to the protons at C-2 (*syn*) and C-6 (*anti*), respectively.

The coupling-constant values between the protons *syn* to the nitroso group ($^3J_{2a,3a}=9.5$ Hz (d), $^3J_{3a,2a}$ and $^3J_{3a,C-3Me}=9.5$, 6.7 Hz (dq)) are comparatively larger than those of the *anti* protons ($^3J_{5a,6a}=3.3$ Hz (d), $^3J_{5a,6a}$ and $^3J_{5a,C-5Me}=3.3$, 7.2 Hz (dq)). The protons at the C-2 and C-3 or C-5 and C-6 positions show a large difference in the coupling-constant values, indicating a significant difference in the dihedral angles involving them. This observation supports a twisted chair conformation of the piperidine ring.

The $^{13}$C NMR spectrum also shows anisochronous behavior of all the carbons in DFMPNO. The signal for the C-2 carbon that is *syn* to the nitroso group appeared at $\delta=53.75$, whereas that for the C-6 carbon *anti* to it occurred at $\delta=61.12$. The methine, methyl and ipso carbons that are *syn* with respect to the nitroso group appeared upfield compared to the carbons *anti* to the nitroso groups.

Stereoviews of the molecules DFMP and DFMPNO are shown in Figs. 1a and 1b, respectively. The atomic parameters of DFMP and DFMPNO are given in Tables 2a and 2b,[17] respectively. The bond distances and

Table 2. Table of Positional Parameters and Their Estimated Standard Deviations

| a) DFMP | | | | | b) DFMPNO | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Atom | $x$ | $y$ | $z$ | $B$/Å$^2$ | Atom | $x$ | $y$ | $z$ | $B$/Å$^2$ |
| N1 | 0.2433(3) | 0.1413(2) | 0.2325(3) | 3.87(5) | N1 | 0.5657(4) | 0.4371(2) | 0.2229(4) | 3.32(8) |
| C2 | 0.2022(3) | 0.0261(2) | 0.2765(4) | 3.76(6) | C2 | 0.4210(5) | 0.4067(2) | 0.2078(6) | 3.5(1) |
| C3 | 0.2815(4) | 0.0299(2) | 0.4890(4) | 4.34(7) | C3 | 0.3546(5) | 0.3970(2) | 0.3914(7) | 3.7(1) |
| C4 | 0.2360(4) | 0.1368(3) | 0.6265(4) | 4.68(7) | C4 | 0.3822(5) | 0.4537(2) | 0.5113(6) | 3.9(1) |
| C5 | 0.2632(4) | 0.2560(3) | 0.5760(4) | 4.83(8) | C5 | 0.5262(5) | 0.4883(2) | 0.5019(6) | 3.7(1) |
| C6 | 0.1882(4) | 0.2430(3) | 0.3606(4) | 4.20(7) | C6 | 0.6331(5) | 0.4515(2) | 0.3884(6) | 3.7(1) |
| C7 | 0.2530(5) | −0.0873(3) | 0.5475(5) | 6.8(1) | C7 | 0.1967(5) | 0.3805(3) | 0.3794(8) | 5.6(1) |
| C8 | 0.2088(6) | 0.3597(4) | 0.7177(6) | 8.3(1) | C8 | 0.5002(7) | 0.5589(2) | 0.4324(8) | 6.3(1) |
| C9 | 0.2229(4) | 0.3567(3) | 0.2999(4) | 5.28(8) | C9 | 0.6907(5) | 0.3918(2) | 0.4759(7) | 4.2(1) |
| O10 | 0.1216(4) | 0.4320(3) | 0.2593(5) | 9.54(9) | O10 | 0.7993(4) | 0.3595(2) | 0.3967(5) | 6.6(1) |
| C11 | 0.2083(6) | 0.5312(3) | 0.2282(6) | 8.5(1) | C11 | 0.8341(6) | 0.3088(3) | 0.5106(9) | 8.0(2) |
| C12 | 0.3485(6) | 0.5084(4) | 0.2426(6) | 9.1(1) | C12 | 0.7537(7) | 0.3100(3) | 0.6476(8) | 6.8(2) |
| C13 | 0.3617(4) | 0.3965(3) | 0.2889(5) | 4.75(7) | C13 | 0.6586(6) | 0.3641(2) | 0.6274(8) | 5.3(1) |
| C14 | 0.2474(3) | −0.0770(2) | 0.1320(4) | 3.96(6) | C14 | 0.4309(5) | 0.3445(2) | 0.1078(7) | 4.5(1) |
| O15 | 0.3979(3) | −0.0739(2) | 0.1114(3) | 5.24(5) | O15 | 0.5139(5) | 0.2957(2) | 0.1651(7) | 9.7(1) |
| C16 | 0.4136(4) | −0.1801(3) | −0.0169(5) | 5.81(8) | C16 | 0.4905(9) | 0.2466(3) | 0.029(1) | 13.1(2) |
| C17 | 0.2825(5) | −0.2483(3) | −0.0735(5) | 5.68(9) | C17 | 0.3941(9) | 0.2679(5) | −0.072(1) | 14.1(2) |
| C18 | 0.1737(4) | −0.1805(3) | 0.0249(5) | 4.92(8) | C18 | 0.3545(7) | 0.3287(3) | −0.0238(8) | 8.5(2) |
| O19 | 0.1753(3) | 0.1285(2) | 0.7672(3) | 6.54(6) | O19 | 0.2942(4) | 0.4709(2) | 0.6171(5) | 6.19(9) |
| | | | | | N20 | 0.6235(4) | 0.4659(2) | 0.0869(6) | 5.0(1) |
| | | | | | O21 | 0.5551(4) | 0.4602(2) | −0.0505(4) | 6.01(9) |

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(4/3)\times[a^2\times B(1,1)+b^2\times B(2,2)+c^2\times B(3,3)+ab(\cos\text{ gamma})\times B(1,2)+ac(\cos\text{ beta})\times B(1,3)+bc(\cos\text{ alpha})\times B(2,3)]$.

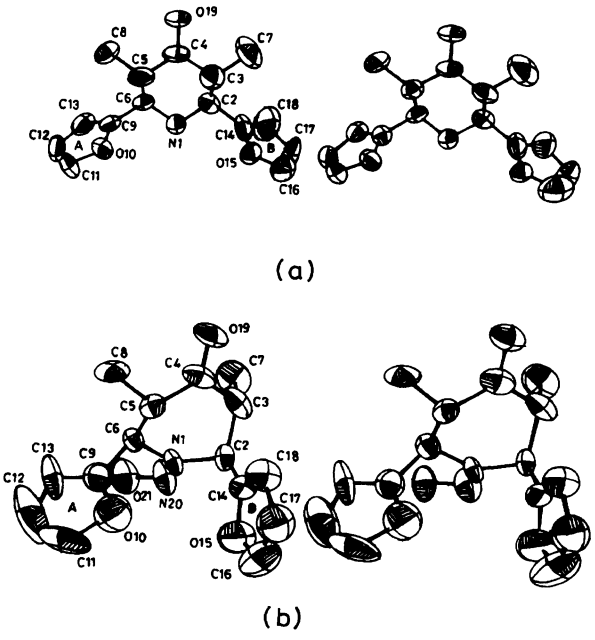



Fig. 1. Stereoview of DFMP (a) and DFMPNO (b). The thermal ellipsoids are drawn at the 50% probability level.

angles are listed in Tables 3a and 3b.

The bond lengths and angles of DFMP and DFMPNO are in agreement with the average values reported in the literature.[18—20] The piperidine ring adopts a chair conformation in DFMP, while it assumes a distorted boat conformation in DFMPNO (Fig. 2) in contrast with an NMR analysis, which indicates that the ring might be in a twisted chair conformation. The different conformation adopted by the piperidine rings indicates that the substituents in DFMP are in a less crowded environment than in DFMPNO. In DFMP, both the methyl groups at the 3- and 5-positions occupy equatorial positions, whereas in DFMPNO they adopt equatorial and axial positions, respectively. The corresponding torsion angles (N1–C2–C3–C7 and N1–C6–C5–C8) are −177.3(3)°, −179.3(3)° for DFMP and 167.3(4)°, −70.4(5)° for DFMPNO.

The furan rings in DFMP and DFMPNO are pla-

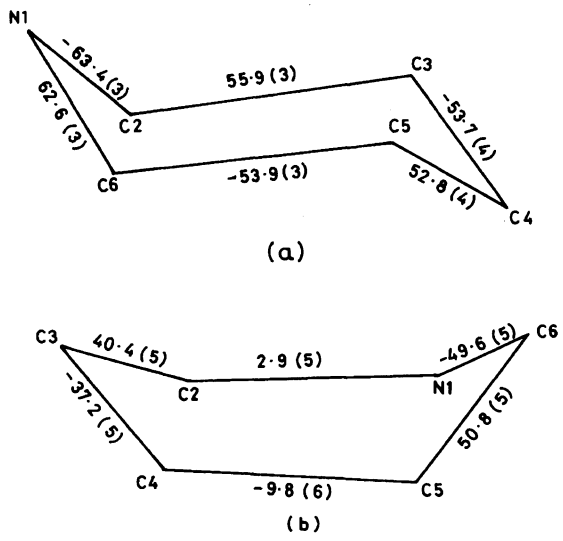



Fig. 2. Chair and distorted boat conformation of (a) DFMP and (b) DFMPNO, respectively.

Table 3. Bond Distances (Å) and Bond Angles (°)

a) DFMP

| Atom 1 | Atom 2 | Distance | Atom 1 | Atom 2 | Distance | Atom 1 | Atom 2 | Distance |
|---|---|---|---|---|---|---|---|---|
| N1 | C2 | 1.466(4) | C4 | O19 | 1.223(4) | C11 | C12 | 1.289(7) |
| N1 | C6 | 1.458(4) | C5 | C6 | 1.546(4) | C12 | C13 | 1.408(6) |
| C2 | C3 | 1.560(4) | C5 | C8 | 1.519(5) | C14 | O15 | 1.370(4) |
| C2 | C14 | 1.488(4) | C6 | C9 | 1.497(4) | C14 | C18 | 1.322(4) |
| C3 | C4 | 1.493(4) | C9 | O10 | 1.338(5) | O15 | C16 | 1.366(4) |
| C3 | C7 | 1.516(5) | C9 | C13 | 1.311(5) | C16 | C17 | 1.319(5) |
| C4 | C5 | 1.509(5) | O10 | C11 | 1.414(5) | C17 | C18 | 1.438(5) |

| Atom 1 | Atom 2 | Atom 3 | Angle | Atom 1 | Atom 2 | Atom 3 | Angle | Atom 1 | Atom 2 | Atom 3 | Angle |
|---|---|---|---|---|---|---|---|---|---|---|---|
| C2 | N1 | C6 | 112.6(2) | C4 | C5 | C6 | 108.7(2) | O10 | C11 | C12 | 107.8(4) |
| N1 | C2 | C3 | 108.7(2) | C4 | C5 | C8 | 112.7(3) | C11 | C12 | C13 | 109.6(4) |
| N1 | C2 | C14 | 111.3(2) | C6 | C5 | C8 | 112.1(3) | C9 | C13 | C12 | 105.3(3) |
| C3 | C2 | C14 | 110.4(2) | N1 | C6 | C5 | 109.5(2) | C2 | C14 | O15 | 117.0(2) |
| C2 | C3 | C4 | 108.1(2) | N1 | C6 | C9 | 110.4(3) | C2 | C14 | C18 | 133.0(3) |
| C2 | C3 | C7 | 113.5(2) | C5 | C6 | C9 | 110.3(2) | O15 | C14 | C18 | 109.8(3) |
| C4 | C3 | C7 | 113.5(3) | C6 | C9 | O10 | 125.6(3) | C14 | O15 | C16 | 106.3(2) |
| C3 | C4 | C5 | 115.7(3) | C6 | C9 | C13 | 122.5(3) | O15 | C16 | C17 | 110.8(3) |
| C3 | C4 | O19 | 122.6(3) | O10 | C9 | C13 | 111.9(3) | C16 | C17 | C18 | 106.0(3) |
| C5 | C4 | O19 | 121.7(3) | C9 | O10 | C11 | 105.3(3) | C14 | C18 | C17 | 107.1(3) |

b) DFMPNO

| Atom 1 | Atom 2 | Distance | Atom 1 | Atom 2 | Distance | Atom 1 | Atom 2 | Distance |
|---|---|---|---|---|---|---|---|---|
| N1 | C2 | 1.493(6) | C4 | O19 | 1.210(6) | C12 | C13 | 1.429(8) |
| N1 | C6 | 1.453(6) | C5 | C6 | 1.527(6) | C14 | O15 | 1.339(6) |
| N1 | N20 | 1.320(5) | C5 | C8 | 1.564(7) | C14 | C18 | 1.282(8) |
| C2 | C3 | 1.558(7) | C6 | C9 | 1.499(6) | O15 | C16 | 1.47(1) |
| C2 | C14 | 1.495(6) | C9 | O10 | 1.357(6) | C16 | C17 | 1.27(1) |
| C3 | C4 | 1.508(6) | C9 | C13 | 1.334(7) | C17 | C18 | 1.35(1) |
| C3 | C7 | 1.515(6) | O10 | C11 | 1.401(7) | N20 | O21 | 1.242(5) |
| C4 | C5 | 1.522(6) | C11 | C12 | 1.296(9) | | | |

| Atom 1 | Atom 2 | Atom 3 | Angle | Atom 1 | Atom 2 | Atom 3 | Angle | Atom 1 | Atom 2 | Atom 3 | Angle |
|---|---|---|---|---|---|---|---|---|---|---|---|
| C2 | N1 | C6 | 123.1(3) | C5 | C4 | O19 | 119.7(4) | O10 | C11 | C12 | 111.2(5) |
| C2 | N1 | N20 | 119.7(3) | C4 | C5 | C6 | 112.0(4) | C11 | C12 | C13 | 106.6(5) |
| C6 | N1 | N20 | 115.4(3) | C4 | C5 | C8 | 108.2(4) | C9 | C13 | C12 | 106.7(5) |
| N1 | C2 | C3 | 110.0(4) | C6 | C5 | C8 | 111.3(4) | C2 | C14 | O15 | 120.3(5) |
| N1 | C2 | C14 | 110.0(4) | N1 | C6 | C5 | 108.7(4) | C2 | C14 | C18 | 126.1(5) |
| C3 | C2 | C14 | 112.6(4) | N1 | C6 | C9 | 112.6(4) | O15 | C14 | C18 | 113.2(5) |
| C2 | C3 | C4 | 113.0(4) | C5 | C6 | C9 | 112.3(4) | C14 | O15 | C16 | 101.0(5) |
| C2 | C3 | C7 | 111.1(4) | C6 | C9 | O10 | 117.7(4) | O15 | C16 | C17 | 107.8(6) |
| C4 | C3 | C7 | 112.1(4) | C6 | C9 | C13 | 131.6(4) | C16 | C17 | C18 | 110.3(8) |
| C3 | C4 | C5 | 118.8(4) | O10 | C9 | C13 | 110.7(4) | C14 | C18 | C17 | 107.3(6) |
| C3 | C4 | O19 | 121.5(4) | C9 | O10 | C11 | 104.7(4) | N1 | N20 | O21 | 115.1(4) |

Numbers in parentheses are estimated standard deviations in the least significant digits.

nar (maximum deviation ±0.038(5) Å and are oriented with respect to each other by 52.6(1)° and 116.1(3)°, respectively. The angles between the best plane of the piperidine ring (C2, C3, C5 and C6 for DFMP and N1, C2, C4, and C5 for DFMPNO) and furan rings A and B are 76.1(2)° and 77.2(1)° for DFMP and 91.3(2)° and 74.5(2)° for DFMPNO. Both of the furan rings are in the equatorial position in DFMP, whereas in DFMPNO ring A is in an axial position and B is in an equatorial position. The corresponding torsion angles (C4–C3–C2–C14 and C4–C5–C6–C9) are 178.3(3)°, −175.7(3)° for DFMP and 163.4(4)°, −74.5(5)° for DFMPNO. A detailed analysis concerning the orientation of the substituents has revealed that the piperidine ring of DFMPNO adopts a boat conformation so as to avoid the bulky groups sticking out on the same side of the molecule, thereby reducing the steric interference.

It has been known from an analysis of the stereochemistry of various derivatives of piperidine that there are two possible orientations for the substituents at the nitrogen, namely planar and perpendicular, regardless of the number of substituents at the 2- and 6-positions with respect to the best plane of the piperidine ring.[10] In DFMPNO, the nitroso group is in the perpendicular orientation. The angle between the nitroso group and the best plane of the piperidine ring is 142.1(4)°. The nitrogen atom is puckered by 0.109(3) Å from the plane formed by the C2, C6, and N20 atoms. The ni-

troso moiety is coplaner with the C2–N1–C6 plane of the piperidine ring, the angle being equal to 166(1)°. The C2–N1–C6 angle is broadened to 123.1(3)° in DFMPNO compared to 112.6(2)° in DFMP because of the partial $sp^2$ character of the piperidine ring nitrogen.

In DFMPNO, the nitroso group is oriented *syn* to C2 (C2–N1–N20–O21 = −6.0(6)°) and *anti* to C6 (C6–N1–N20–O21 = −171.3(4)°). This can be called a *syn–anti* conformation.[21]

A detailed analysis of X-ray studies indicate that all observations are in conformity with the NMR results, except for the conformation of the piperidine ring in DFMPNO.

The primary interaction between the molecules is van der Waals in nature in DFMP and DFMPNO. The shortest intermolecular distances between the molecules are [N1···O19 ($x$, $y$, $z-1$)=] 3.237(3) Å in DFMP and [C2···O19 ($-x+1/2$, $-y+1$, $z-1/2$)=] 3.290(6) Å in DFMPNO.

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