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# The Crystal and Molecular Structures of 3-Methyl-4-nitropyridine *N*-Oxide and 3,5-Dimethyl-4-nitropyridine *N*-Oxide

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The crystal structures of 3-methyl-4-nitropyridine *N*-oxide (M4NPO), tetragonal 3,5-dimethyl-4-nitropyridine *N*-oxide (D4NPO-T) and orthorhombic D4NPO (D4NPO-O) have been determined. M4NPO is orthorhombic, space group $P2_12_12_1$, $a = 21·359$ (2), $b = 6·111$ (1), $c = 5·132$ (1) Å, $Z = 4$. D4NPO-T is tetragonal, space group $P4_12_12$, $a = 7·443$ (1), $c = 13·447$ (1) Å, $Z = 4$. D4NPO-O is orthorhombic, space group *Pbca*, $a = 7·329$ (1), $b = 14·912$ (2), $c = 13·852$ (2) Å, $Z = 8$. The intensity data were collected on a four-circle diffractometer by use of Zr-filtered Mo $K\alpha$ radiation. The structures were refined by a block-diagonal least-squares method to $R = 0·062$ for M4NPO (661 reflexions), 0·051 for D4NPO-T (472) and 0·085 for D4NPO-O (941). The twist angles of the nitro group out of the molecular plane are 16·7, 49·4 and 51·1°, and the N—O distances of the *N*-oxide group are 1·292 (1·299 after libration corrections), 1·289 (1·293) and 1·302 (1·306) Å in the order given above. The contribution of the quinoid structure to the resonance forms is significant in the two molecules, as in 4-nitropyridine *N*-oxide. The intramolecular charge transfer from the *N*-oxide group O atom to the nitro group plays an important role in stabilizing these molecules in less-twisted conformations than those of their related compounds.

## Introduction

The studies of the absorption spectra of 4-nitropyridine *N*-oxide (4NPO), 3-methyl-4-nitropyridine *N*-oxide (M4NPO) and 3,5-dimethyl-4-nitropyridine *N*-oxide (D4NPO) have been reported (Yamakawa, Kubota, Ezumi & Mizuno, 1974). The nitro groups in M4NPO and D4NPO are twisted out of the molecular planes because of the steric effects of the methyl groups substituted at their vicinal positions. The charge transfer (CT) band of D4NPO is remarkably different (decreased in intensity) from those of the other two compounds, which are almost the same. The twist angles were estimated to be 0, 11·2 and 55·5° for 4NPO, M4NPO and D4NPO respectively. In the 3-methyl and 3,5-dimethyl derivatives of 4NPO and 4-nitroaminobenzene, the twist angles are smaller than those in the corresponding derivatives of 4-nitrobenzene. It was hence pointed out that the intramolecular CT between the nitro group and the substituent at its *p*-position influenced the twist angle; the twist decreases with increasing CT.

The structure of 4NPO has been reported by Eichhorn (1956) and refined at 30 and 300 K by Wang, Blessing, Ross & Coppens (1976). The structure analyses of M4NPO and D4NPO were undertaken to see how the effect of the intramolecular CT from the *N*-oxide group O atom to the nitro group operates on the molecular structure.

## Experimental

The crystals of each compound were recrystallized by slow evaporation from an acetone solution. Those of D4NPO were obtained in two crystalline polymorphous forms; one is tetragonal (D4NPO-T) and the other orthorhombic (D4NPO-O). Preliminary X-ray

Table 1. *Crystal data for M4NPO, D4NPO-T and D4NPO-O*

| | M4NPO | D4NPO-T | D4NPO-O |
|---|---|---|---|
| | $C_6H_6N_2O_3$ | $C_7H_8N_2O_3$ | $C_7H_8N_2O_3$ |
| FW | 154·1 | 168·2 | 168·2 |
| *a* | 21·359 (2) Å | 7·443 (1) Å | 7·329 (1) Å |
| *b* | 6·111 (1) | 7·443 (1) | 14·912 (2) |
| *c* | 5·132 (1) | 13·447 (1) | 13·852 (2) |
| *U* | 669·8 Å$^3$ | 745·0 Å$^3$ | 1514·0 Å$^3$ |
| $D_x$ | 1·53 g cm$^{-3}$ | 1·50 g cm$^{-3}$ | 1·48 g cm$^{-3}$ |
| $D_m$ (flotation) | 1·55 | 1·51 | 1·50 |
| *Z* | 4 | 4 | 8 |
| Crystal size | 0·3 × 0·3 × 0·3 mm | 0·3 × 0·3 × 0·3 mm | 0·2 × 0·2 × 0·2 mm |
| Linear absorption coefficient (Mo $K\alpha$) | 1·52 cm$^{-1}$ | 1·44 cm$^{-1}$ | 1·42 cm$^{-1}$ |
| Systematically absent reflexions | | | |
| $0kl$ | | | $k = 2n + 1$ |
| $h0l$ | | | $l = 2n + 1$ |
| $hk0$ | | | $h = 2n + 1$ |
| $h00$ | $h = 2n + 1$ | $h = 2n + 1$ | ($h = 2n + 1$) |
| $0k0$ | $k = 2n + 1$ | | ($k = 2n + 1$) |
| $00l$ | $l = 2n + 1$ | $l \neq 4n$ | ($l = 2n + 1$) |
| Space group | $P2_12_12_1$ | $P4_12_12$ | *Pbca* |
| Number of reflexions measured ($\theta_{ma}$ | 772 (25·5°) | 480 (27·5°) | 1345 (25·0°) |

photographs gave space group and approximate unit-cell dimensions. Accurate cell constants were obtained from a least-squares fit of 12 reflexions measured by diffractometer. Crystal data are given in Table 1.

Three-dimensional intensity data were collected on a Hilger & Watts Y-290 diffractometer equipped with a scintillation counter and pulse-height analyser. Integrated intensities were measured by the $\theta$–$2\theta$ scan technique by use of Zr-filtered Mo $K\alpha$ radiation. Each reflexion was integrated in 80 steps at intervals of 0·01° $s^{-1}$. Backgrounds were counted for 20 s on both sides of each reflexion. One standard reflexion monitored every 10 reflexions showed no significant change in intensity during data collection. All intensities were corrected for Lorentz and polarization factors, but not for absorption effects.

Intensity data for D4NPO-T were collected in two equivalent regions, and corresponding structure factors in these sets were then averaged to give the unique reflexion data for the tetragonal crystal. The structure factors for which the differences were larger than $3\sigma$ were not used in the structure refinement.

## Structure determination and refinement

### *M*4*NPO*

The structure was solved by use of the program *MULTAN* (Main, Germain & Woolfson, 1970) with local modifications on a FACOM 270-30 computer. In the $E$ map based on the set of phases with the highest figure-of-merit, all the non-hydrogen atoms were located. 115 $E$ values ($E \geq 1{\cdot}5$) were used for the calculation of the $E$ map. After the coordinates and isotropic temperature factors of these atoms were refined by a block-diagonal least-squares method a difference electron-density map was calculated, in which all the H atoms were found in positions not far from those expected on chemical grounds. The temperature factor of each H atom was assumed to be isotropic and equal to that of the C atom to which it was bound. The positional and thermal parameters of the H atoms were fixed in the subsequent refinements. After anisotropic refinement on the non-hydrogen atoms, a difference electron-density map was calculated, again excluding the contributions of the H atoms, in which no significant peaks other than those due to the H atoms were found. The final refinement gave an $R$ value, where $R = \Sigma|\Delta F|/\Sigma|F_o|$, of 0·062 for 661 reflexions.*

### *D*4*NPO-T*

The molecules were assumed to lie on twofold axes in the crystal. The structure was solved by a group least-squares method, a rigid-body molecule of $C_2$ molecular symmetry being used. The coordinates of the centre of mass ($x$,$x$,0), the rotation angle of the whole molecule and that of the nitro group were refined. One of the trials led to a successful structure, the $R$ value converging to 0·19 for 35 reflexions ($\theta \leq 10°$). After introducing the H atoms the refinement reduced $R$ to 0·12, though one more rotation angle for the methyl group was added as a parameter to be refined. The positional parameters of all the atoms and the anisotropic thermal parameters of the non-hydrogen atoms were then refined by a block-diagonal least-squares method, the isotropic thermal parameters of the H atoms being fixed. The final $R$ value was 0·051 for 472 reflexions.*

### *D*4*NPO-O*

The structure was solved by the method of Beurskens (1963) with a program written for a FACOM 270-30 computer. The $E$ map based on the signs of 248 reflexions ($E \geq 1{\cdot}0$) revealed the positions of all the non-hydrogen atoms. The structure was refined as for M4NPO and the $R$ value converged to 0·085 for 941 reflexions.*

The standard deviation of each reflexion was taken as $\sigma(F_o) = [\sigma_1^2(F_o) + c^2|F_o|^2]^{1/2}$, where $\sigma_1(F_o)$ is the estimated standard deviation (e.s.d.) depending on the counting errors (Grant, Killean & Lawrence, 1969). The final values of $c^2$ were 0·00125, 0·00168 and 0·00095 for M4NPO, D4NPO-T and D4NPO-O respectively. The function minimized in the refinement was $\Sigma\,(w|\Delta F|^2)$, and the weighting scheme used was $w = 1/\sigma^2(F_o)$ for $|F_c| \geq \sigma(F_o)$ and $w = 0$ for $|F_c| < \sigma(F_o)$ or $|\Delta F| > 3\sigma(F_o)$. The values $[\Sigma(w|\Delta F|^2)/(m - n)]^{1/2}$, where $m$ is the number of structure factors in the summation and $n$ is the number of variables, were 1·124, 1·116 and 1·167 in the order given above. The final parameter shifts were sufficiently small compared with the e.s.d. values of the parameters. The atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1962).

## Results and discussion

Fig. 1 shows the atom-numbering system of each molecule. The positional and thermal parameters with their e.s.d. values are given in Tables 2, 3 and 4. Respective crystal structures are shown in Figs. 2, 3 and 4, and short intermolecular distances are listed in Table 5.

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32286 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

* See first footnote.

Table 2. *Atomic fractional coordinates* ($\times 10^4$) *and thermal parameters* (Å$^2$ $\times 10^3$) *for M4NPO*

The anisotropic temperature factor is of the form: $\exp[-2\pi^2(U_{11}a^{*2}h^2 + U_{22}b^{*2}k^2 + U_{33}c^{*2}l^2 + 2U_{12}a^*b^*hk + 2U_{13}a^*c^*hl + 2U_{23}b^*c^*kl)]$.

| | $x$ | $y$ | $z$ | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{12}$ | $U_{13}$ | $U_{23}$ |
|---|---|---|---|---|---|---|---|---|---|
| N(1) | 1541 (1) | 490 (5) | 86 (7) | 48 (3) | 37 (2) | 58 (2) | 1 (2) | −10 (2) | 9 (2) |
| C(2) | 1797 (2) | 1792 (6) | −1789 (9) | 39 (3) | 40 (2) | 52 (2) | 0 (2) | −3 (2) | 7 (2) |
| C(3) | 1519 (2) | 3715 (6) | −2551 (7) | 41 (3) | 38 (2) | 33 (2) | −8 (2) | −4 (2) | 0 (2) |
| C(4) | 969 (2) | 4293 (6) | −1303 (7) | 32 (3) | 35 (2) | 43 (2) | −1 (2) | −8 (2) | 1 (2) |
| C(5) | 716 (2) | 2996 (6) | 653 (8) | 37 (3) | 44 (2) | 45 (2) | −4 (2) | 3 (2) | −2 (2) |
| C(6) | 1010 (2) | 1089 (7) | 1333 (8) | 47 (3) | 49 (2) | 46 (2) | −7 (2) | 0 (2) | 5 (2) |
| O(7) | 1808 (1) | −1337 (5) | 698 (7) | 67 (3) | 48 (2) | 90 (3) | 12 (2) | −8 (2) | 21 (2) |
| C(8) | 1869 (2) | 5039 (7) | −4556 (8) | 47 (3) | 51 (3) | 50 (2) | −4 (2) | 3 (2) | 10 (2) |
| N(10) | 622 (1) | 6288 (6) | −1947 (7) | 43 (3) | 48 (2) | 56 (2) | −1 (2) | −3 (2) | 4 (2) |
| O(11) | 746 (2) | 7206 (5) | −3987 (7) | 71 (3) | 81 (2) | 82 (2) | 23 (2) | 12 (2) | 48 (2) |
| O(12) | 225 (1) | 6928 (5) | −448 (7) | 61 (3) | 62 (2) | 72 (2) | 20 (2) | 11 (2) | −8 (2) |

| | $x$ | $y$ | $z$ | $U$ | | $x$ | $y$ | $z$ | $U$ |
|---|---|---|---|---|---|---|---|---|---|
| H(C2) | 2240 | 1170 | −2710 | 42 | H(C8) | 2340 | 4420 | −4750 | 47 |
| H(C5) | 240 | 3460 | 1460 | 41 | H′(C8) | 1470 | 5210 | −6040 | 47 |
| H(C6) | 730 | 0 | 2830 | 48 | H″(C8) | 1930 | 6500 | −3960 | 47 |

Table 3. *Atomic fractional coordinates* ($\times 10^4$) *and thermal parameters* (Å$^2$ $\times 10^4$) *for D4NPO-T*

Anisotropic temperature factor: $\exp[-2\pi^2(U_{11}a^{*2}h^2 + U_{22}b^{*2}k^2 + U_{33}c^{*2}l^2 + 2U_{12}a^*b^*hk + 2U_{13}a^*c^*hl + 2U_{23}b^*c^*kl)]$.

| | $x$ | $y$ | $z$ | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{12}$ | $U_{13}$ | $U_{23}$ |
|---|---|---|---|---|---|---|---|---|---|
| N(1) | 3683 (3) | 3683 (3) | 0 | 351 (11) | 351 (11) | 459 (18) | −3 (7) | −22 (5) | 22 (5) |
| C(2) | 2025 (4) | 4045 (3) | 372 (2) | 405 (14) | 304 (11) | 406 (9) | 32 (6) | −34 (6) | −7 (5) |
| C(3) | 697 (3) | 2771 (4) | 390 (2) | 314 (11) | 342 (14) | 331 (9) | 27 (6) | −8 (5) | 6 (5) |
| C(4) | 1091 (3) | 1091 (3) | 0 | 299 (11) | 299 (11) | 298 (18) | 10 (8) | 4 (5) | −4 (5) |
| O(7) | 4907 (3) | 4907 (3) | 0 | 408 (8) | 408 (8) | 737 (18) | −63 (7) | −30 (5) | 30 (5) |
| C(8) | −1077 (4) | 3267 (5) | 861 (2) | 377 (14) | 510 (17) | 527 (18) | 40 (7) | 23 (6) | −56 (8) |
| N(10) | −304 (3) | −304 (3) | 0 | 370 (11) | 370 (11) | 351 (18) | −15 (7) | 5 (5) | −5 (5) |
| O(11) | −1790 (3) | 100 (3) | −314 (1) | 326 (8) | 609 (14) | 603 (9) | −19 (5) | −20 (5) | 20 (5) |

| | $x$ | $y$ | $z$ | $U$ | | $x$ | $y$ | $z$ | $U$ |
|---|---|---|---|---|---|---|---|---|---|
| H(C2) | 1870 (50) | 5200 (60) | 520 (30) | 350 | H′(C8) | −970 (50) | 4440 (60) | 1230 (30) | 455 |
| H(C8) | −1820 (50) | 3520 (50) | 380 (30) | 455 | H″(C8) | −1450 (50) | 2350 (50) | 1270 (30) | 455 |

Table 4. *Atomic fractional coordinates* ($\times 10^4$) *and thermal parameters* (Å$^2$ $\times 10^3$) *for D4NPO-O*

Anisotropic temperature factor: $\exp[-2\pi^2(U_{11}a^{*2}h^2 + U_{22}b^{*2}k^2 + U_{33}c^{*2}l^2 + 2U_{12}a^*b^*hk + 2U_{13}a^*c^*hl + 2U_{23}b^*c^*kl)]$.

| | $x$ | $y$ | $z$ | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{12}$ | $U_{13}$ | $U_{23}$ |
|---|---|---|---|---|---|---|---|---|---|
| N(1) | 6318 (5) | 3205 (2) | 1018 (2) | 37 (2) | 42 (2) | 34 (2) | −2 (2) | −3 (2) | 4 (2) |
| C(2) | 4672 (6) | 3452 (3) | 1368 (3) | 39 (3) | 59 (3) | 33 (3) | −5 (3) | −1 (2) | −5 (2) |
| C(3) | 3340 (6) | 3787 (3) | 775 (3) | 36 (2) | 37 (2) | 34 (2) | −8 (2) | 2 (2) | −5 (2) |
| C(4) | 3739 (6) | 3864 (3) | −203 (3) | 39 (2) | 31 (2) | 34 (2) | −4 (2) | −2 (2) | −1 (2) |
| C(5) | 5434 (6) | 3619 (3) | −579 (3) | 38 (2) | 37 (2) | 35 (3) | −4 (2) | 2 (2) | −6 (2) |
| C(6) | 6698 (6) | 3290 (3) | 63 (3) | 32 (2) | 48 (3) | 47 (3) | −6 (2) | 2 (2) | −6 (3) |
| O(7) | 7565 (4) | 2892 (2) | 1596 (2) | 43 (2) | 66 (2) | 49 (2) | 6 (2) | −17 (2) | 5 (2) |
| C(8) | 1556 (7) | 4081 (3) | 1221 (3) | 43 (3) | 62 (3) | 46 (3) | 6 (3) | 6 (3) | −6 (3) |
| C(9) | 5937 (7) | 3651 (3) | −1631 (3) | 59 (3) | 67 (3) | 35 (3) | −7 (3) | 13 (3) | 1 (3) |
| N(10) | 2310 (5) | 4203 (3) | −861 (2) | 46 (2) | 43 (2) | 35 (2) | 1 (2) | −1 (2) | 1 (2) |
| O(11) | 800 (4) | 3961 (2) | −809 (2) | 36 (2) | 67 (2) | 63 (2) | −9 (2) | −7 (2) | 9 (2) |
| O(12) | 2711 (5) | 4804 (2) | −1407 (2) | 75 (2) | 59 (2) | 55 (2) | 0 (2) | −4 (2) | 21 (2) |

| | $x$ | $y$ | $z$ | $U$ | | $x$ | $y$ | $z$ | $U$ |
|---|---|---|---|---|---|---|---|---|---|
| H(C2) | 4420 | 3400 | 2040 | 37 | H″(C8) | 1830 | 4120 | 1960 | 49 |
| H(C6) | 7920 | 3100 | −140 | 40 | H(C9) | 7250 | 3400 | −1780 | 49 |
| H(C8) | 1080 | 4680 | 1080 | 49 | H′(C9) | 5000 | 3400 | −2040 | 49 |
| H′(C8) | 670 | 3600 | 1100 | 49 | H″(C9) | 5790 | 4240 | −1900 | 49 |

Table 5. *Short intermolecular distances* (Å) *for M4NPO, D4NPO-T and D4NPO-O*

The Roman numerals as superscripts refer to the equivalent positions relative to the reference molecule at ($x,y,z$).

M4NPO

(i) $x, 1+y, -1+z$
(ii) $x, -1+y, z$
(iii) $x, y, -1+z$
(iv) $\frac{1}{2}-x, -y, \frac{1}{2}+z$
(v) $-x, -\frac{1}{2}+y, -\frac{1}{2}-z$
(vi) $-x, -\frac{1}{2}+y, \frac{1}{2}-z$

| | | | |
|---|---|---|---|
| O(11)–C($6^{i}$) | 3·424 | O(7)–O($12^{ii}$) | 3·592 |
| C(8)–O($7^{i}$) | 3·295 | O(11)–O($12^{iii}$) | 3·502 |
| N(1)–N($10^{ii}$) | 3·397 | O(7)–C($2^{iv}$) | 3·259 |
| N(1)–O($11^{ii}$) | 3·359 | C(4)–O($12^{v}$) | 3·372 |
| N(1)–O($12^{ii}$) | 3·567 | C(5)–O($12^{v}$) | 3·406 |
| C(6)–O($12^{ii}$) | 3·181 | C(5)–O($11^{v}$) | 3·274 |
| O(7)–C($4^{ii}$) | 3·375 | N(10)–O($12^{v}$) | 3·487 |
| O(7)–N($10^{ii}$) | 3·218 | C(6)–O($12^{vi}$) | 3·417 |
| O(7)–O($11^{ii}$) | 3·422 | C(5)–O($12^{vi}$) | 3·243 |

D4NPO-T

(i) $1+x, y, z$
(ii) $\frac{1}{2}-y, \frac{1}{2}+x, \frac{1}{4}+z$
(iii) $-\frac{1}{2}-y, \frac{1}{2}+x, \frac{1}{4}+z$
(iv) $\frac{1}{2}-y, -\frac{1}{2}+x, \frac{1}{4}+z$
(v) $\frac{1}{2}+y, \frac{1}{2}-x, -\frac{1}{4}+z$
(vi) $y, 1+x, -z$
(vii) $-\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{4}-z$

| | | | |
|---|---|---|---|
| O(7)–C($8^{i}$) | 3·429 | C(8)–O($11^{iii}$) | 3·485 |
| N(1)–O($11^{ii}$) | 3·096 | C(3)–O($7^{iv}$) | 3·578 |
| C(2)–C($4^{ii}$) | 3·532 | C(4)–O($7^{iv}$) | 3·554 |
| C(2)–O($11^{ii}$) | 3·304 | O(7)–C($8^{v}$) | 3·446 |
| O(7)–N($10^{ii}$) | 3·378 | C(2)–O($11^{vi}$) | 3·416 |
| O(7)–O($11^{ii}$) | 3·200 | C(8)–O($11^{vii}$) | 3·359 |

D4NPO-O

(i) $\frac{1}{2}+x, \frac{1}{2}-y, -z$
(ii) $-\frac{1}{2}+x, \frac{1}{2}-y, -z$
(iii) $1+x, y, z$
(iv) $1-x, 1-y, -z$
(v) $x, \frac{1}{2}-y, \frac{1}{2}+z$
(vi) $-\frac{1}{2}+x, y, \frac{1}{2}-z$
(vii) $\frac{1}{2}+x, y, \frac{1}{2}-z$
(viii) $\frac{1}{2}+x, y, -\frac{1}{2}-z$

| | | | |
|---|---|---|---|
| N(1)–O($11^{i}$) | 3·117 | C(2)–O($12^{iv}$) | 3·231 |
| O(7)–C($9^{i}$) | 3·377 | O(7)–O($12^{iv}$) | 3·451 |
| O(7)–N($10^{i}$) | 3·291 | O(7)–C($9^{v}$) | 3·572 |
| O(7)–O($11^{i}$) | 3·114 | C(2)–O($7^{vi}$) | 3·322 |
| C(4)–O($7^{ii}$) | 3·365 | O(7)–C($8^{vii}$) | 3·583 |
| C(5)–O($7^{ii}$) | 3·389 | C(9)–O($11^{viii}$) | 3·562 |
| O(7)–C($8^{iii}$) | 3·460 | C(9)–O($12^{viii}$) | 3·469 |
| N(1)–O($12^{iv}$) | 3·100 | | |

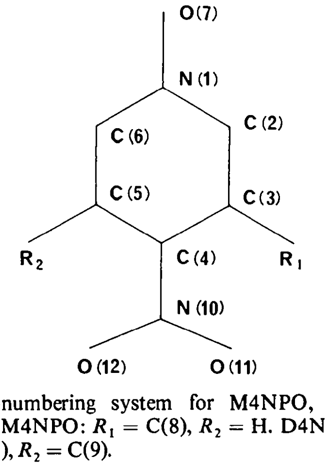

Fig. 1. Atom-numbering system for M4NPO, D4NPO-T and D4NPO-O. M4NPO: $R_1$ = C(8), $R_2$ = H. D4NPO-T, D4NPO-O: $R_1$ = C(8), $R_2$ = C(9).

As shown in Fig. 5, the intermolecular contacts between the *N*-oxide and nitro groups (type 1) seem to be important in these crystals. A net charge calculation by the CNDO/2 method (Pople & Beveridge, 1970) showed that each N–O can be regarded as a partial dipole and hence these contacts result from dipole–dipole attractions between the N–O bonds belonging to different

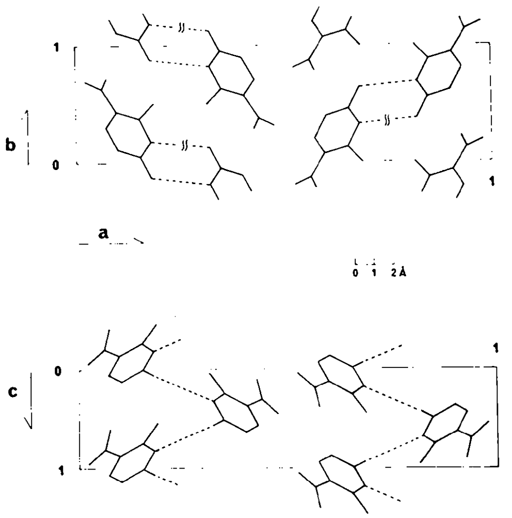

Fig. 2. Crystal structure of M4NPO.

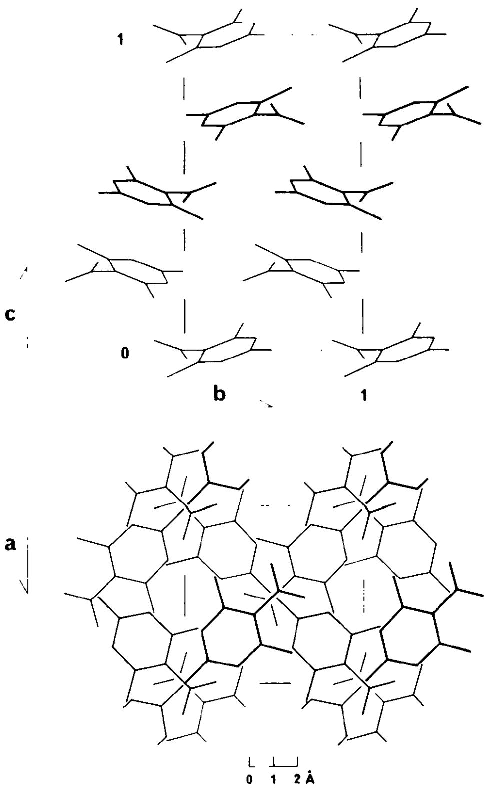

Fig. 3. Crystal structure of D4NPO-T.

groups. Other short contacts between the *N*-oxide group O atoms and C—H of pyridine rings (type 2) are found in M4NPO and D4NPO-O, which are indicated by dashed lines in Figs. 2 and 4. The C—H bonds point approximately to the O atoms, and O · · · C distances are 3·259 and 3·322 Å respectively. Short approaches of the same type have been observed in 4NPO and the 2:1 molecular complex between 4NPO and hydroquinone (Shiro & Kubota, 1972). The crystals of M4NPO and D4NPO-O may be described as consisting of layers which are stacked in the directions of the *a* (M4NPO) and *c* axes (D4NPO-O). Short intermolecular contacts of type 1 are observed in the layer and those of type 2 between different layers. In the crystal of D4NPO-T, a three-dimensional network of cross-linked molecules with short contacts of type 1 is formed.

Moreover, near-perpendicular contacts between O atoms and pyridine C atoms are observed: 3·181 and 3·274 in M4NPO, 3·304 in D4NPO-T, and 3·231 Å in D4NPO-O. The angles between the C · · · O vector and the pyridine plane are 60, 49, 68 and 73° corresponding to the order given above. A similar contact is seen in the light-sensitive ($\alpha$) form of *p*-nitrophenol, but not in the light-stable ($\beta$) form of it (Coppens & Schmidt, 1964). The crystals of D4NPO-T and D4NPO-O discolour from yellow to red under sunlight, which might correspond to the photochemical phenomenon in light-sensitive *p*-nitrophenol in the solid state.

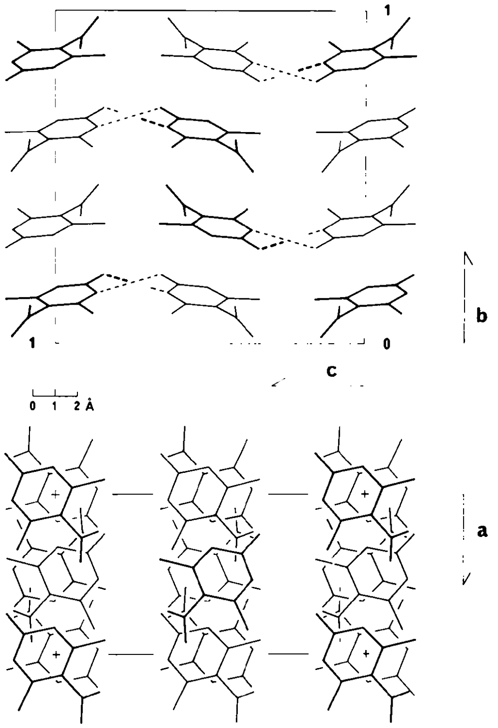

Fig. 4. Crystal structure of D4NPO-O.

The results of the rigid-body thermal motion analysis are given in Table 6. In D4NPO-T and D4NPO-O, the major libration axis lies along the minor inertial axis of the D4NPO molecule (strictly or approximately in the direction of the long molecular axis), as in 4NPO, but the anisotropy of the libration motion is not so significant as in 4NPO.

The bond lengths and angles involving only non-hydrogen atoms are listed in Tables 7 and 8, and the least-squares planes in Table 9. The molecular dimensions of D4NPO in the crystals of D4NPO-T and D4NPO-O are equal within experimental error. The bond lengths observed in the M4NPO and D4NPO molecules are in good correlation with the bond orders calculated by CNDO/2. The nitro groups are displaced from the molecular plane with dihedral angles of 16·7 (M4NPO) and 50·3° (D4NPO; mean of the angles obtained in D4NPO-T and D4NPO-O), which are similar to the angles estimated by Yamakawa *et al.* (1974). The bond angles around C(3) and C(4) in M4NPO are largely deformed to reduce the repulsive interactions between the nitro and methyl groups. The shortest contact is 2·23 Å in O(11) · · · H′(C8). Such non-bonded distances are longer than 2·5 Å in D4NPO-T and D4NPO-O.

In the pyridine ring of D4NPO, the C—C bonds parallel to the long molecular axis are shorter than the other C—C, and the N—C bond lengths are close to those in pyridine *N*-oxide [microwave spectroscopy $l =$ 1·362 Å (Snerling, Nielsen, Nygaard, Pedersen & Sørensen, 1975); gas-phase electron diffraction $l =$ 1·384 Å (Chiang, 1974)] rather than to those in pyridine itself [microwave spectroscopy $l =$ 1·338 Å (Sørensen, Mahler & Rastrup-Andersen, 1974)]. A similar trend is found in M4NPO. These indicate that the contribution of the quinoid structure to the resonance forms is significant in the molecules of M4NPO and D4NPO as well as in 4NPO.

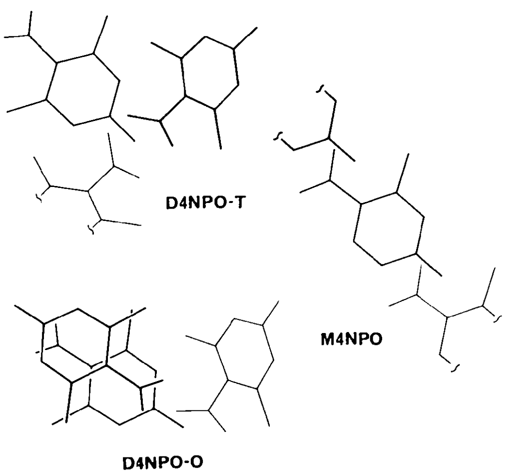

Fig. 5. Projections vertical to respective molecular planes for M4NPO, D4NPO-T and D4NPO-O.

Table 6. *Rigid-body thermal parameters*

Molecular axes 1, 2 and 3 are taken along the minor, intermediate and major inertial axes of the molecule respectively.

| | M4NPO | | | D4NPO-T | | | D4NPO-O | | |
|---|---|---|---|---|---|---|---|---|---|
| Direction cosines of the molecular axes relative to the crystal axes (× $10^4$) | | | | | | | | | |
| | 1 | 2 | 3 | 1 | 2 | 3 | 1 | 2 | 3 |
| *a* | −4436 | −7034 | 5554 | 7071 | 6572 | −2609 | 7033 | −6472 | −2941 |
| *b* | 8535 | −1424 | 5013 | 7071 | −6572 | 2609 | −3549 | 387 | −9341 |
| *c* | −2735 | 6963 | 6636 | 0 | −3690 | −9294 | 6160 | 7613 | −2025 |
| $[\Sigma(\Delta U_{ij})^2/(m-n)]^{1/2}$ (Å$^2$) | | | | | | | | | |
| | | 0·0090 | | | 0·0035 | | | 0·0053 | |
| Molecular vibration tensors | | | | | | | | | |
| Translation (× $10^3$ Å$^2$) | | | | | | | | | |
| | 38 (3) | 2 (3) | 2 (3) | 35 (1) | 0 (1) | 0 (1) | 39 (2) | −2 (2) | 3 (2) |
| | | 39 (4) | 2 (4) | | 32 (1) | 3 (1) | | 33 (2) | −2 (2) |
| | | | 29 (5) | | | 26 (2) | | | 26 (3) |
| Libration (× $10^4$ rad$^2$) | | | | | | | | | |
| | 44 (19) | 16 (9) | −7 (12) | 44 (5) | 0 (4) | 0 (3) | 57 (8) | −6 (6) | −4 (5) |
| | | 68 (8) | −8 (7) | | 36 (3) | −2 (3) | | 41 (5) | 1 (4) |
| | | | 36 (6) | | | 21 (2) | | | 30 (3) |
| Principal axes of the tensors | | | | | | | | | |
| Translation | | | | | | | | | |
| R.m.s. amplitude (Å) | | | | | | | | | |
| | 0·17 | 0·19 | 0·20 | 0·16 | 0·18 | 0·19 | 0·16 | 0·18 | 0·20 |
| Direction cosines relative to the molecular axes (× $10^4$) | | | | | | | | | |
| 1 | −1917 | 7549 | 6272 | 0 | 0 | 10000 | −2115 | 3774 | 9016 |
| 2 | −1247 | −6526 | 7474 | −3358 | 9307 | 0 | 1842 | 9213 | −3425 |
| 3 | 9735 | 651 | 2192 | 9307 | 3658 | 0 | 9599 | −936 | 2644 |
| Libration | | | | | | | | | |
| R.m.s. oscillation angles (°) | | | | | | | | | |
| | 3·2 | 3·5 | 5·1 | 2·6 | 3·5 | 3·8 | 3·1 | 3·6 | 4·4 |
| Direction cosines relative to the molecular axes (× $10^4$) | | | | | | | | | |
| 1 | 5236 | 7235 | 4500 | 0 | 0 | 10000 | 1534 | 3185 | 9354 |
| 2 | −440 | −5045 | 8623 | 1565 | 9877 | 0 | −197 | 9474 | −3194 |
| 3 | 8508 | −4713 | −2323 | 9877 | −1565 | 0 | 9880 | −306 | −1517 |

Table 7. *Bond lengths* (Å) *for M4NPO, D4NPO-T and D4NPO-O*

Mean estimated standard deviations are 0·005, 0·003 and 0·006 Å respectively. The values in the second row for each bond are corrected for libration effects.

| | M4NPO | D4NPO-T | D4NPO-O | | M4NPO | D4NPO-T | D4NPO-O |
|---|---|---|---|---|---|---|---|
| N(1)—O(7) | 1·292 | 1·289 | 1·302 | C(4)—C(5) | 1·389 | | 1·395 |
| | 1·299 | 1·293 | 1·306 | | 1·396 | | 1·401 |
| N(1)—C(2) | 1·363 | 1·359 | 1·352 | C(3)—C(8) | 1·508 | 1·510 | 1·510 |
| | 1·370 | 1·364 | 1·357 | | 1·515 | 1·516 | 1·516 |
| N(1)—C(6) | 1·353 | | 1·357 | C(5)—C(9) | | | 1·504 |
| | 1·358 | | 1·363 | | | | 1·511 |
| C(2)—C(3) | 1·374 | 1·370 | 1·370 | C(4)—N(10) | 1·464 | 1·468 | 1·477 |
| | 1·381 | 1·375 | 1·375 | | 1·472 | 1·473 | 1·482 |
| C(5)—C(6) | 1·369 | | 1·375 | N(10)—O(11) | 1·217 | 1·222 | 1·221 |
| | 1·376 | | 1·380 | | 1·223 | 1·226 | 1·226 |
| C(3)—C(4) | 1·383 | 1·387 | 1·391 | N(10)—O(12) | 1·211 | | 1·210 |
| | 1·388 | 1·393 | 1·397 | | 1·216 | | 1·216 |

Table 8. *Bond angles* (°) *for M4NPO, D4NPO-T and D4NPO-O*

Mean estimated standard deviations are 0·3, 0·2 and 0·4° respectively.

| | M4NPO | D4NPO-T | D4NPO-O |
|---|---|---|---|
| C(2)—N(1)—O(7) | 120·0 | 120·1 | 120·2 |
| C(6)—N(1)—O(7) | 119·2 | | 119·3 |
| C(2)—N(1)—C(6) | 120·8 | 119·8 | 120·5 |
| N(1)—C(2)—C(3) | 121·8 | 121·6 | 121·4 |
| C(2)—C(3)—C(4) | 117·0 | 117·7 | 117·6 |
| C(3)—C(4)—C(5) | 121·3 | 121·6 | 122·0 |
| C(4)—C(5)—C(6) | 119·5 | | 116·9 |
| N(1)—C(6)—C(5) | 119·6 | | 121·7 |
| C(2)—C(3)—C(8) | 116·0 | 118·0 | 118·6 |
| C(4)—C(3)—C(8) | 126·9 | 124·3 | 123·8 |
| C(6)—C(5)—C(9) | | | 118·2 |
| C(4)—C(5)—C(9) | | | 124·9 |
| C(3)—C(4)—N(10) | 122·5 | 119·2 | 118·7 |
| C(5)—C(4)—N(10) | 116·2 | | 119·3 |
| C(4)—N(10)—O(11) | 118·7 | 117·8 | 117·6 |
| C(4)—N(10)—O(12) | 117·9 | | 117·9 |
| O(11)—N(10)—O(12) | 123·4 | 124·4 | 124·5 |

Table 9. *Equations of the least-squares planes and deviations* (Å) *of the atoms from the planes*

The equation of the plane is of the form: $AX + BY + CZ = D$, where $A$, $B$ and $C$ are the direction cosines relative to the respective crystal axes, $X$, $Y$ and $Z$, which are measured in Å.

| | M4NPO | D4NPO-T | D4NPO-O |
|---|---|---|---|
| N(1), C(2), C(3), C(4), C(5), C(6), O(7), C(8), C(9), N(10) | | | |
| *A* | 0·5208 | 0·3145 | 0·3489 |
| *B* | 0·4858 | −0·3145 | 0·9264 |
| *C* | 0·7020 | 0·8956 | 0·1420 |
| *D* | 1·8930 | 0·0000 | 6·2498 |
| N(1) | −0·002 | 0·000 | −0·007 |
| C(2) | −0·007 | −0·025 | −0·018 |
| C(3) | −0·020 | −0·017 | −0·012 |
| C(4) | −0·010 | 0·000 | 0·004 |
| C(5) | 0·028 | 0·017 | 0·025 |
| C(6) | 0·034 | 0·025 | 0·019 |
| O(7) | −0·028 | 0·000 | −0·006 |
| C(8) | 0·040 | 0·019 | 0·026 |
| C(9) | | −0·019 | −0·009 |
| N(10) | −0·036 | 0·000 | −0·023 |
| C(4), N(10), O(11), O(12) | | | |
| *A* | 0·6879 | −0·2761 | −0·2697 |
| *B* | 0·5503 | 0·2761 | 0·6740 |
| *C* | 0·4733 | 0·9206 | 0·6878 |
| *D* | 2·5521 | 0·0000 | 2·9504 |
| C(4) | −0·001 | 0·000 | 0·001 |
| N(10) | 0·004 | 0·000 | −0·003 |
| O(11) | −0·001 | 0·000 | 0·001 |
| O(12) | −0·001 | 0·000 | 0·001 |
| Angle between the two planes | | | |
| | 16·7° | 49·4° | 51·1° |

Table 10. *Comparison of N-oxide* N—O *distances* (Å)

The data without any description of the experimental technique were obtained by the X-ray diffraction method. The values in brackets were corrected for libration effects. The N—O forming a hydrogen bond is asterisked.

| | |
|---|---|
| Pyridine *N*-oxide | |
| 1·290 (15) | electron diffraction; Chiang (1974) |
| 1·278 (10) | microwave spectroscopy; Snerling *et al.* (1975) |
| 1·33 (2), 1·37 (2) | Ülkü, Huddle & Morrow (1971) (two independent molecules in the asymmetric unit) |
| 4NPO | |
| 1·297 (1) [1·297] | at 30 K Wang *et al.* (1976) |
| 1·298 (2) [1·304] | at 300 K |
| 1·288 | neutron diffraction |
| 2 : 1 molecular complex between 4NPO and hydroquinone | |
| 1·310 (4)* | Shiro & Kubota (1972) |
| M4NPO | |
| 1·292 (5) [1·299] | present work |
| D4NPO | |
| 1·289 (3) [1·293] | in D4NPO-T present work |
| 1·302 (6) [1·306] | in D4NPO-O |
| 2-Hydroxymethylpyridine *N*-oxide | |
| 1·321 (2)* | Desiderato & Terry (1971) |
| 8-Hydroxyquinoline *N*-oxide | |
| 1·333 (2)* | Desiderato, Terry, Freeman & Levy (1971) |
| *N*-Oxyphenazine | |
| 1·24 (2) | Curti, Riganti & Locchi (1961) |
| 1-Hydroxy-6-methoxyphenazine 5,10-dioxide (myxin) | |
| 1·318 (4)* [1·325] | Hanson (1968) |
| 1·273 (4) [1·287] | (two independent molecules in the |
| 1·313 (4)* [1·321] | asymmetric unit) |
| 1·280 (4) [1·288] | |
| 1,6-Dihydroxyphenazine 5,10-dioxide (iodinin) | |
| 1·306 (3)* | Hanson & Huml (1969) (molecules at inversion points) |
| 4,4-*trans*-Azopyridine *N*-oxide | |
| 1·283 (11) | Eichhorn (1959) |

Table 11. N—O *bond orders and bond lengths of N-oxide group in* 4*NPO as functions of the twist angle* ($NO_2$)

The bond orders were calculated by the SCF–MO method. The bond order–length relation is $1/l^2 = (p-1)/1\cdot16^2 - (p-2)/1\cdot415^2$, where $p$ is the bond order and $l$ the bond length (Kubota, 1959).

| Twist angle (°) | 0 | 20 | 40 | 60 | 80 | 90 |
|---|---|---|---|---|---|---|
| Bond order | 1·4432 | 1·4423 | 1·4399 | 1·4369 | 1·4347 | 1·4344 |
| Bond length (Å) | 1·283 | 1·283 | 1·284 | 1·285 | 1·285 | 1·285 |

The N—O distances in the *N*-oxide groups are listed in Table 10. They are evidently lengthened in the presence of hydrogen bonding. The N—O lengths are as expected, though those in M4NPO and D4NPO-O would be affected by the C—H · · · O interactions as described above. 4NPO forms a molecular complex with hydroquinone (HQ) in a 2:1 molecular ratio, one HQ being connected to two inversely related 4NPO molecules by two hydrogen bonds (O···O = 2·690 Å). In the 1:1 M4NPO-HQ and 2:3 D4NPO-HQ molecular complexes, hydrogen bonds of the same type are found (to be published by the authors).

In the 4NPO molecule, strong CT occurs from the *N*-oxide group O atom to the nitro group *via* the pyridine ring, especially in the $\pi$–$\pi^*$ excited state (intramolecular CT absorption band) (Yamakawa *et al.*, 1974). Such CT varies as the square of the cosine of the twist angle of the nitro group. Changes of the N—O bond order in the *N*-oxide group in the ground state were calculated as a function of the twist angle by the SCF–MO method (Table 11). The bond lengths estimated from the bond orders tend to lengthen in very twisted conformations, but little variation is observed. There are, in fact, no differences larger than $2\sigma$ among the N—O distances observed in 4NPO, M4NPO, D4NPO-T and D4NPO-O.

In D4NPO, nitromesitylene (Trotter, 1959) and 3,5-dimethyl-4-nitrobenzoic acid (Apreda, Smith-Verdier & Garcia-Blanco, 1973), the twist angles of the nitro group are 50·3, 66 and 86·3° respectively, and the intramolecular CT from the *p*-substituent to the nitro group decreases in that order. It is suggested that the CT contributes to stabilize the D4NPO molecule in a relatively less-twisted conformation.

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