5-Cyanotropolone and 5-nitro-tropolone

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The title compounds, 4-hydroxy-5-oxo-1,3,6-cycloheptatriene-1-carbonitrile, $C_8H_5NO_2$, (I), and 2-hydroxy-5-nitro-2,4,6-cycloheptatrien-1-one, $C_7H_5NO_4$, (II), have intra- and intermolecular hydrogen bonds. The structure of (II) contains two crystallographically independent molecules, (IIa) and (IIb). An intermolecular π–π interaction and an intermolecular $NO_2\cdots\pi$–π interaction are present in (I) and (II), respectively.

Comment

Troponoids have been an important building block for the construction of liquid crystals (Mori *et al.*, 1992; Mori & Takeshita, 1995), ionophores (Mori *et al.*, 1996; Kubo *et al.*, 1999) and dyes (Takeshita *et al.*, 1989; Mori *et al.*, 1993). The troponoid moiety plays an important role in generating new properties in molecular assemblies. Recently, we have prepared liquid crystals with a tropolone core such as 5-hydroxy- (Mori & Takeshita, 1995), 5-phenyl- (Mori *et al.*, 1992), 5-nitro- and 5-cyanotropolones (Hashimoto *et al.*, 2000). The cores enhanced formation of smectic phases when compared with the corresponding benzenoids. The crystal structure analyses of tropolone (Shimanouchi & Sasada, 1973) and of metal complexes, such as copper (Berg *et al.*, 1978) and
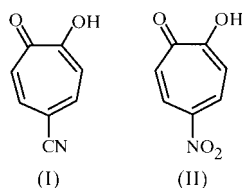
iron (Hamor & Watkin, 1969), of tropolones have been carried out. However, the crystal structures of 5-hydroxy-, 5-phenyl-, 5-nitro- and 5-cyanotropolone have not been elucidated. We now report the structures of 5-cyano- and 5-nitrotropolone, (I) and (II), respectively, with the aim of contributing to a deeper understanding of troponoids and molecular assemblies.

The structure of (II) contains two crystallographically independent molecules, (IIa) and (IIb), related by a non-

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crystallographic screw axis in the *a*-axis direction located at $(x, \frac{1}{4}, \frac{1}{2})$. The planarities of (I) (Fig. 1) and (II) (Fig. 2) are fairly good; the deviations of atoms from the least-squares plane of (I), (IIa), and (IIb) are within 0.03 (1), 0.07 (2) and 0.23 (2) Å, respectively. The C—C bond-length patterns of the seven-membered ring of (I), (IIa) and (IIb) are similar to those of tropolone (Shimanouchi & Sasada, 1973).

Compounds (I) and (II) form hydrogen-bonded dimers about inversion centres, involving the OH group and an intermolecular component, with the carbonyl O1 atom being the acceptor in both cases. These bonds are tabulated in Tables 2 and 4, and illustrated in Figs. 3 and 4. The distances are close to that of tropolone (2.746 Å). Intermolecular π–π interactions between the tropolone dimer planes (head-to-head) of (I) and between the tropolone dimer planes (head-to-tail) of (II) are observed. The distance between intermolecular tropolone planes is 3.791 (5) Å for $C1\cdots C1^{iv}$ [symmetry code: (iv) $x, y, z - 1$] in (I) and 3.399 (2) Å for $C1\cdots C5^{v}$ [symmetry
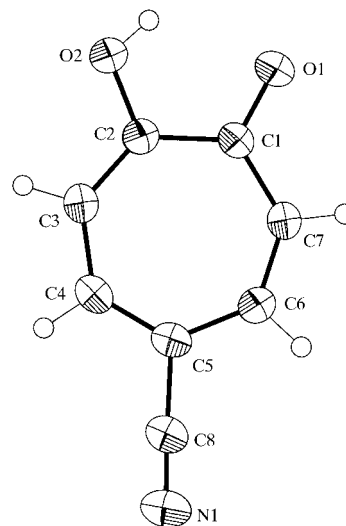

Figure 1
The molecular structure of (I) showing 50% probability displacement ellipsoids.
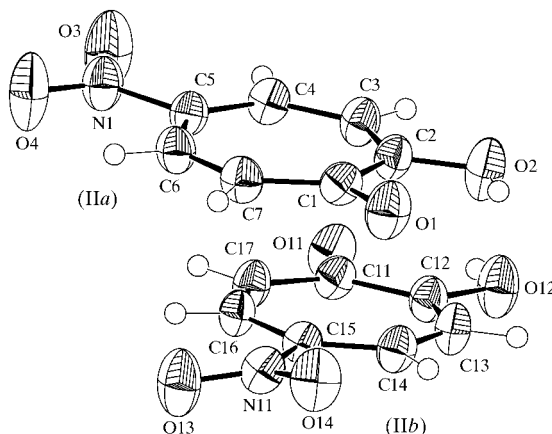

Figure 2
The molecular structures of the two molecules of (II) showing 50% probability displacement ellipsoids.
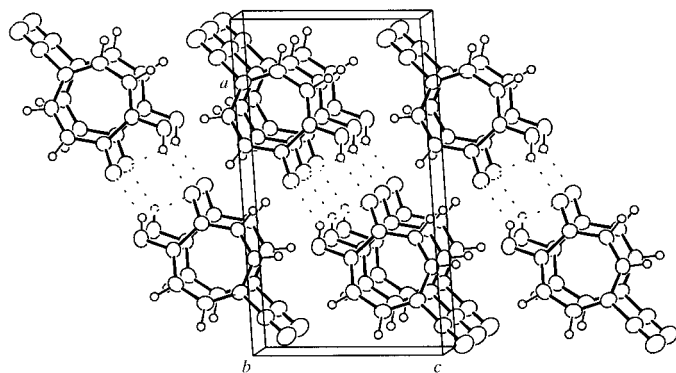
organic compounds

Figure 3
Packing diagram of (I) viewed approximately down the *b* axis, with hydrogen bonds shown as dotted lines.

code: (v) $-x, 1 - y, 1 - z$] in (II), which are within the range associated with π–π interactions (3.3–3.8 Å). The values are similar to that (3.715 Å) of the intermolecular C1$\cdots$C3^{vi} [symmetry code: (vi) $1 + x, \frac{1}{2} - y, \frac{1}{2} + z$] interaction of tropolone (Shimanouchi & Sasada, 1973) and the π–π packing of (I) and (II) are distinct from that of tropolone (Shimanouchi & Sasada, 1973).

Intermolecular interaction between a nitro group and a seven-membered ring of (II) is observed; 3.611 (2) Å for C7$\cdots$N11, 3.602 (2) Å for C6$\cdots$O13 and 3.123 (2) Å for C1$\cdots$O14. Thus, the substituent at C5 differentiated the crystal packing in the lattice.
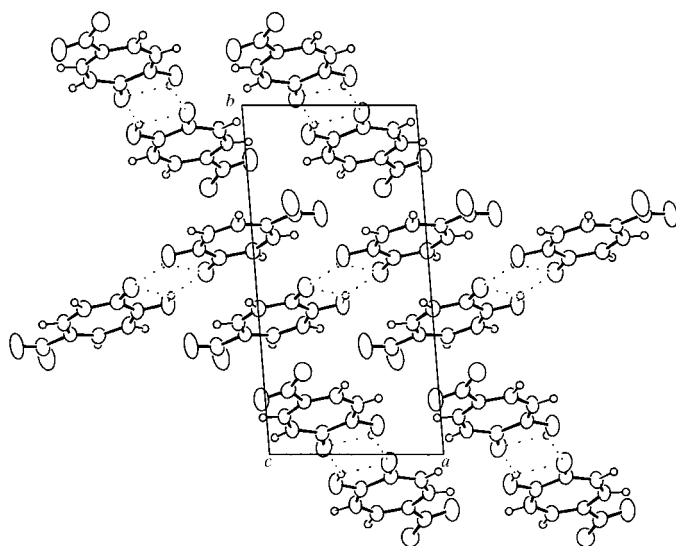

Figure 4
Packing diagram of (II) viewed down the *c* axis, with hydrogen bonds shown as dotted lines.

Experimental

Compound (I) was synthesized by diazotization and cyanation of 5-aminotropolone (Cook *et al.*, 1954). Compound (II) was synthesized by the nitration of tropolone (Doering & Knox, 1951). Single crystals of (I) and (II) were obtained by recrystallization from chloroform.

Compound (I)

Crystal data

$C_8H_5NO_2$	$Z = 2$
$M_r = 147.13$	$D_x = 1.443$ Mg m^{-3}
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 7.1995$ (5) Å	Cell parameters from 25
$b = 12.6309$ (14) Å	reflections
$c = 3.7913$ (3) Å	$\theta = 6.8$–18.4°
$\alpha = 90.805$ (9)°	$\mu = 0.106$ mm^{-1}
$\beta = 99.905$ (7)°	$T = 296$ (2) K
$\gamma = 94.116$ (8)°	Prism, yellow
$V = 338.63$ (5) Å^3	$0.53 \times 0.30 \times 0.13$ mm

Data collection

Enraf–Nonius CAD-4 diffractometer	$R_{int} = 0.011$
	$\theta_{max} = 27.97°$
ω–2θ scans	$h = -9 \rightarrow 9$
Absorption correction: ψ scan (North *et al.*, 1968)	$k = -16 \rightarrow 16$
	$l = -4 \rightarrow 0$
$T_{min} = 0.918$, $T_{max} = 0.986$	3 standard reflections
1854 measured reflections	frequency: 120 min
1611 independent reflections	intensity decay: 2.2%
1311 reflections with $I > 2\sigma(I)$	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o{}^2) + (0.0569P)^2 + 0.0600P]$
$R[F^2 > 2\sigma(F^2)] = 0.036$	
$wR(F^2) = 0.106$	where $P = (F_o{}^2 + 2F_c{}^2)/3$
$S = 1.033$	$(\Delta/\sigma)_{max} < 0.001$
1611 reflections	$\Delta\rho_{max} = 0.28$ e Å^{-3}
102 parameters	$\Delta\rho_{min} = -0.14$ e Å^{-3}
H-atom parameters constrained	Extinction correction: *SHELXL*97 (Sheldrick, 1997)
	Extinction coefficient: 0.120 (17)

Table 1
Selected bond lengths (Å) for (I).

N1—C8	1.1377 (18)	C3—C4	1.3984 (18)
O1—C1	1.2468 (14)	C4—C5	1.3750 (18)
O2—C2	1.3330 (15)	C5—C6	1.4175 (17)
C1—C7	1.4294 (17)	C5—C8	1.4461 (16)
C1—C2	1.4704 (16)	C6—C7	1.3588 (17)
C2—C3	1.3716 (17)		

Table 2
Hydrogen-bonding geometry (Å, °) for (I).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O2—H2$\cdots$O1^{i}	0.82	2.05	2.761 (2)	145
O2—H2$\cdots$O1	0.82	2.08	2.563 (2)	118

Symmetry code: (i) $1 - x, 1 - y, 1 - z$.

Compound (II)

Crystal data

$C_7H_5NO_4$	$Z = 4$
$M_r = 167.12$	$D_x = 1.617$ Mg m^{-3}
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 7.5701$ (10) Å	Cell parameters from 25
$b = 14.496$ (3) Å	reflections
$c = 6.4945$ (7) Å	$\theta = 10.8$–18.3°
$\alpha = 90.751$ (14)°	$\mu = 0.136$ mm^{-1}
$\beta = 104.796$ (8)°	$T = 296$ (2) K
$\gamma = 94.410$ (13)°	Prism, yellow
$V = 686.7$ (2) Å^3	$0.40 \times 0.30 \times 0.23$ mm

Data collection

Enraf–Nonius CAD-4 diffractometer	$R_{int} = 0.009$
ω–2θ scans	$\theta_{max} = 27.97°$
Absorption correction: ψ scan (North *et al.*, 1968)	$h = -9 \rightarrow 9$
	$k = -19 \rightarrow 0$
$T_{min} = 0.914$, $T_{max} = 0.969$	$l = -8 \rightarrow 8$
3438 measured reflections	3 standard reflections
3309 independent reflections	frequency: 120 min
2493 reflections with $I > 2\sigma(I)$	intensity decay: 0.5%

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0603P)^2 + 0.1579P]$
$R[F^2 > 2\sigma(F^2)] = 0.039$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.119$	$(\Delta/\sigma)_{max} < 0.001$
$S = 1.026$	$\Delta\rho_{max} = 0.29$ e Å^{-3}
3309 reflections	$\Delta\rho_{min} = -0.18$ e Å^{-3}
220 parameters	Extinction correction: *SHELXL*97 (Sheldrick, 1997)
H-atom parameters constrained	Extinction coefficient: 0.141 (9)

Table 3
Selected bond lengths (Å) for (II).

N1—O4	1.2117 (18)	N11—O13	1.2205 (17)
N1—O3	1.2139 (18)	N11—O14	1.2220 (17)
N1—C5	1.4800 (19)	N11—C15	1.4796 (17)
O1—C1	1.2411 (17)	O11—C11	1.2463 (17)
O2—C2	1.3268 (18)	O12—C12	1.3317 (17)
C1—C7	1.435 (2)	C11—C17	1.433 (2)
C1—C2	1.478 (2)	C11—C12	1.474 (2)
C2—C3	1.370 (2)	C12—C13	1.366 (2)
C3—C4	1.401 (2)	C13—C14	1.405 (2)
C4—C5	1.361 (2)	C14—C15	1.3626 (19)
C5—C6	1.4096 (19)	C15—C16	1.4012 (19)
C6—C7	1.359 (2)	C16—C17	1.3620 (19)

Table 4
Hydrogen-bonding geometry (Å, °) for (II).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O2—H2$\cdots$O1^i	0.82	2.05	2.743 (2)	142
O2—H2$\cdots$O1	0.82	2.10	2.586 (2)	117
O12—H12$\cdots$O11^{ii}	0.82	2.07	2.771 (2)	143
O12—H12$\cdots$O11	0.82	2.09	2.573 (2)	118

Symmetry codes: (i) $1 - x, 1 - y, 2 - z$; (ii) $1 - x, -y, -z$.

All H atoms were located at ideal positions with C—H = 0.93 Å and O—H = 0.82 Å, and restrained with U_{iso} held fixed at 1.2U_{eq} of the parent atoms.

For both compounds, data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989); cell refinement: *CAD*-4 *Software*; data reduction: *MolEN* (Fair, 1990); program(s) used to solve structure: *SIR*97 (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *Xtal_GX* (Hall & du Boulay, 1995); software used to prepare material for publication: *SHELXL*97.

References

Altomare, A., Burla, M. C., Camalli, M., Cascarano, G. L., Giacovazzo, C., Guagliardi, A., Moliterni, A. G. G., Polidori, G. & Spagna, R. (1999). *J. Appl. Cryst.* **32**, 115–119.

Berg, J. E., Pilotti, A. M., Soderholm, A. C. & Karlsson, B. (1978). *Acta Cryst.* B**34**, 3071–3072.

Cook, J. W., Loudon, J. D. & Steel, D. K. V. (1954). *J. Chem. Soc.* pp. 530–535.

Doering, W. von E. & Knox, L. H. (1951). *J. Am. Chem. Soc.* **73**, 828–838.

Enraf–Nonius (1989). *CAD-4 Software*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.

Fair, C. K. (1990). *MolEN*. Enraf–Nonius, Delft, The Netherlands.

Hall, S. R. & du Boulay, D. (1995). *Xtal_GX*. University of Western Australia, Australia.

Hamor, T. A. & Watkin, D. J. (1969). *J. Chem. Soc. D*, **9**, 440–441.

Hashimoto, M., Ujiie, S. & Mori, A. (2000). *Chem. Lett.* pp. 758–759.

Kubo, K., Yamamoto, E., Kato, N. & Mori, A. (1999). *Acta Cryst*, C**55**, 1819–1821.

Mori, A., Kanemasa, S., Fujimoto, E., Wada, E., Takeshita, H., Kato, N. & Mori, A. (1993). *Heterocycles*, **35**, 869–878.

Mori, A., Katahira, K., Kida, K. & Takeshita, H. (1992). *Chem. Lett.* pp. 1767–1770.

Mori, A., Kubo, K. & Takeshita, H. (1996). *Coord. Chem. Rev.* **148**, 71–96.

Mori, A. & Takeshita, H. (1995). *J. Synth. Org. Chem. Jpn*, **53**, 197–206.

North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.

Sheldrick, G. M. (1997). *SHELXL*97. University of Göttingen, Germany.

Shimanouchi, H. & Sasada, Y. (1973). *Acta Cryst.* B**29**, 81–90.

Takeshita, H., Mori, A., Nagao, T. & Nagamura, T. (1989). *Chem. Lett.* **10**, 1719–1722.