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cis-2,3,4aβ,8aβ-Tetramethyl-4a,5,8,8a-tetrahydro-1,4-naphthoquinone (TTN), $C_{14}H_{18}O_2$, and *cis*-2,3,4aβ,8aβ-Tetramethyl-4a,5,6,7,8,8a-hexahydro-1,4-naphthoquinone (THN), $C_{14}H_{20}O_2$

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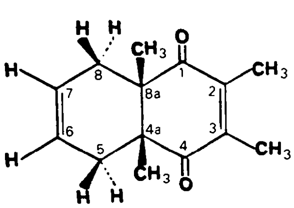
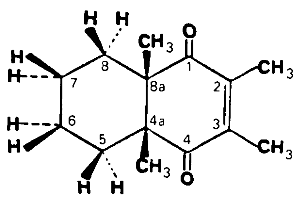
Abstract. TTN, THN: $M_r = 218{\cdot}30$, $220{\cdot}31$, orthorhombic, *Pbca*, $a = 26{\cdot}255$ (2), $26{\cdot}699$ (4), $b = 10{\cdot}387$ (1), $10{\cdot}413$ (1), $c = 8{\cdot}966$ (1), $9{\cdot}003$ (1) Å, $V = 2445{\cdot}2$ (5), $2502{\cdot}9$ (5) Å^3, $Z = 8$, $D_x = 1{\cdot}186$, $1{\cdot}169$ g cm^{-3}, $T = 295$ K, Mo $K\alpha$, $\lambda(K\alpha_1) = 0{\cdot}70930$ Å, $\mu = 0{\cdot}764$, $0{\cdot}761$ cm^{-1}, $F(000) = 944$, 960, final $R = 0{\cdot}081$, $0{\cdot}073$, for 1905, 939 observed reflections, respectively. The crystals are isostructural. In both structures the cyclohexene (TTN) and cyclohexane (THN) moieties are *cis*-fused to a half-chair cyclohex-2-ene-1,4-dione ring. In the TTN molecule the cyclohexene ring exists in a half-chair conformation, in the THN molecule the cyclohexane ring adopts a chair conformation.

Introduction. The similarity between the solid-state ^{13}C NMR spectra of TTN (I) and THN (II) (J. R. Scheffer & Y. F. Wong, private communication) suggests that these two molecules crystallize in isostructural lattices. The present crystallographic study was undertaken to establish their crystal structures and to determine the similarity between their molecular conformations.



(I)



(II)

Experimental. TTN and THN crystals from ethanol. D_m not determined. TTN m.p. 317–320 K, $0{\cdot}5 \times 0{\cdot}5 \times 0{\cdot}3$ mm; THN m.p. 315–317 K, $0{\cdot}2 \times 0{\cdot}2 \times 0{\cdot}5$ mm (mounted in a capillary tube because of air sensitivity). CAD-4 diffractometer, graphite-monochromatized Mo $K\alpha$ radiation. Lattice parameters from setting of 25 reflections with $15 \le \theta \le 22°$. 3054 unique reflections with $\theta \le 27°$ for TTN, 2552 with $\theta \le 25°$ for THN. ω–2θ scan for TTN, ω–$5/3\theta$ for THN, ω scan width $(0{\cdot}6 + 0{\cdot}3\tan\theta)°$ for TTN, $(0{\cdot}8 + 0{\cdot}3\tan\theta)°$ for THN, extended 25% on each side for background measurement, horizontal aperture $(1{\cdot}0 + \tan\theta)$mm, vertical aperture 4 mm. Lp corrections, no absorption corrections. Three standard reflections, 10% decay for TTN, stable for THN. Structures solved by direct methods using *SHELX* (Sheldrick, 1976) and refined by full-matrix least-squares minimizing $\sum w(|F_o| - |F_c|)^2$, 217 parameters consisting of 102 positional parameters, 96 anisotropic temperature factors, 18 isotropic temperature factors and a scale factor for TTN; 165 parameters consisting of 60 positional parameters, 96 anisotropic temperature factors, 8 isotropic temperature factors and a scale factor for THN. H atoms from a difference synthesis for TTN, but calculated for THN. Final $R = 0{\cdot}081$, $R_w = 0{\cdot}090$ for 1905 reflections for TTN, final R

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Table 1. *Atomic coordinates* ($\times 10^4$) *and thermal parameters* ($Å^2 \times 10^3$)

U_{eq} is one third the trace of the diagonalized anisotropic temperature factor matrix.

	x	y	z	U_{eq}
TTN				
O(1)	773 (1)	511 (4)	654 (4)	75
O(4)	1951 (1)	−757 (4)	−3889 (4)	72
C(1)	1023 (2)	123 (5)	−393 (5)	49
C(2)	1517 (2)	−510 (5)	−136 (5)	49
C(3)	1831 (2)	−787 (5)	−1290 (6)	48
C(4)	1696 (2)	−377 (4)	−2831 (6)	45
C(4a)	1269 (2)	586 (4)	−3038 (5)	41
C(4a1)	1499 (2)	1913 (5)	−2652 (8)	60
C(5)	1087 (2)	595 (5)	−4651 (6)	53
C(6)	765 (2)	−539 (6)	−5040 (7)	63
C(7)	556 (2)	−1294 (6)	−4074 (6)	61
C(8)	619 (2)	−1132 (5)	−2406 (6)	50
C(8a)	821 (1)	220 (4)	−1990 (5)	42
C(8a1)	382 (2)	1193 (6)	−2062 (8)	61
C(21)	1649 (3)	−836 (8)	1458 (7)	79
C(31)	2328 (2)	−1484 (8)	−1090 (9)	72
THN				
O(1)	799 (1)	391 (4)	770 (3)	99
O(4)	1980 (1)	−694 (3)	−3756 (3)	78
C(1)	1054 (2)	75 (4)	−303 (5)	60
C(2)	1546 (2)	−522 (4)	−49 (5)	57
C(3)	1853 (1)	−772 (4)	−1186 (5)	52
C(4)	1715 (1)	−358 (4)	−2720 (5)	51
C(4a)	1276 (1)	542 (3)	−2942 (4)	45
C(4a1)	1488 (2)	1899 (4)	−2644 (5)	68
C(5)	1096 (2)	469 (4)	−4559 (4)	59
C(6)	863 (2)	−828 (4)	−4967 (5)	65
C(7)	450 (2)	−1203 (4)	−3888 (4)	65
C(8)	635 (1)	−1144 (4)	−2278 (4)	56
C(8a)	846 (1)	189 (4)	−1864 (4)	48
C(8a1)	425 (2)	1193 (5)	−1876 (5)	77
C(21)	1684 (2)	−832 (5)	1555 (4)	85
C(31)	2349 (2)	−1454 (5)	−1015 (5)	81

$= 0.073$, $R_w = 0.05$ for 939 reflections for THN, for which $F \geq 3\sigma(F)$, where $\sigma^2(I) = S + 2B + [0.04(S-B)]^2$, $S =$ scan count, $B =$ time-averaged background count. $R = 0.124$, $R_w = 0.140$ for TTN, $R = 0.150$, $R_w = 0.058$ for THN for all data, $w = 1/\sigma^2(F)$, ± 0.30 e $Å^{-3}$ for TTN, ± 0.26 e $Å^{-3}$ for THN in final difference synthesis. Atomic scattering factors from Cromer & Mann (1968) and Stewart, Davidson & Simpson (1965). Final $(\Delta/\sigma)_{max}$ 0·26 for TTN, 0·04 for THN.

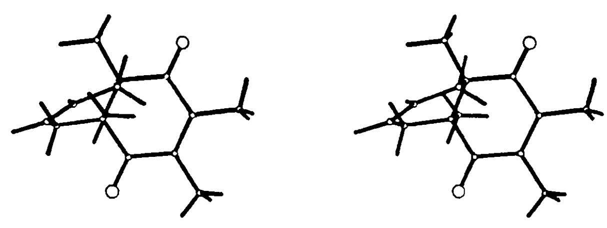
Discussion. Final atomic coordinates are in Table 1,* bond distances and bond angles in Table 2.

A stereodiagram of the TTN and THN molecules is shown in Fig. 1. The crystal lattices of TTN and THN are isostructural and both molecules adopt similar conformations consisting of a half-chair cyclohexene (TTN) and a chair cyclohexane (THN) ring *cis*-fused to a half-chair cyclohexenedione moiety. The conformation is seen to be twisted around the C(4a)—C(8a) bond such that the bridgehead methyl groups are staggered. The degree of 'twist' is shown by the torsion angles C(5)—C(4a)—C(8a)—C(1) and C(4a1)—C(4a)—C(8a)—C(8a1) of 176·0 (4) and 59·8 (5) (TTN) and 171·6 (3) and 54·6 (4)° (THN).

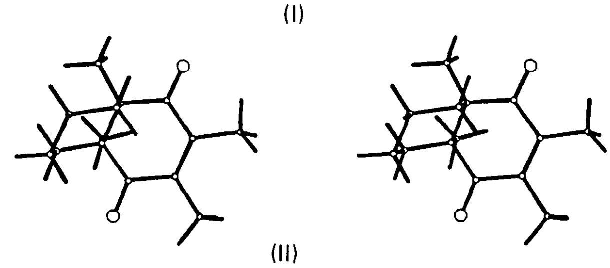
* Lists of structure factors, anisotropic thermal parameters, and coordinates, bond distances and angles involving hydrogen atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39211 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Interatomic distances* (Å) *and angles* (°)

	TTN	THN
C(1)—O(1)	1·214 (5)	1·227 (4)
C(4)—O(4)	1·226 (5)	1·222 (4)
C(1)—C(2)	1·474 (6)	1·470 (5)
C(2)—C(3)	1·354 (6)	1·337 (5)
C(3)—C(4)	1·488 (6)	1·493 (5)
C(4)—C(4a)	1·514 (6)	1·513 (5)
C(4a)—C(5)	1·523 (6)	1·535 (5)
C(5)—C(6)	1·492 (7)	1·532 (5)
C(6)—C(7)	1·290 (7)	1·520 (5)
C(7)—C(8)	1·513 (7)	1·533 (5)
C(8)—C(8a)	1·548 (6)	1·544 (5)
C(1)—C(8a)	1·530 (6)	1·517 (5)
C(4a)—C(8a)	1·552 (6)	1·548 (5)
C(2)—C(21)	1·509 (8)	1·526 (5)
C(3)—C(31)	1·504 (7)	1·511 (5)
C(4a)—C(4a1)	1·544 (6)	1·546 (5)
C(8a)—C(8a1)	1·535 (6)	1·535 (5)
C(2)—C(1)—O(1)	120·2 (4)	119·2 (4)
C(1)—C(2)—C(3)	120·8 (4)	120·7 (4)
C(2)—C(3)—C(4)	120·3 (4)	120·0 (4)
C(3)—C(4)—C(4a)	118·6 (4)	119·5 (3)
C(3)—C(4)—O(4)	119·8 (4)	118·7 (4)
C(4a)—C(4)—O(4)	121·5 (4)	121·6 (4)
C(4)—C(4a)—C(5)	110·6 (4)	109·8 (3)
C(4a)—C(5)—C(6)	113·3 (4)	113·5 (3)
C(5)—C(6)—C(7)	124·3 (5)	111·6 (4)
C(6)—C(7)—C(8)	123·3 (5)	111·1 (3)
C(7)—C(8)—C(8a)	112·1 (4)	112·4 (3)
C(2)—C(1)—C(8a)	118·7 (4)	120·3 (4)
C(4a)—C(8a)—C(1)	108·7 (3)	109·1 (3)
C(8)—C(8a)—C(4a)	109·7 (3)	109·4 (3)
C(8a)—C(1)—O(1)	121·0 (4)	120·3 (4)
C(8a)—C(4a)—C(4)	109·0 (3)	110·2 (3)
C(8a)—C(4a)—C(5)	109·8 (3)	110·5 (3)
C(8)—C(8a)—C(1)	106·5 (4)	106·6 (3)
C(1)—C(2)—C(21)	116·7 (5)	116·9 (4)
C(21)—C(2)—C(3)	122·5 (5)	122·3 (4)
C(31)—C(3)—C(2)	122·6 (5)	123·5 (4)
C(31)—C(3)—C(4)	117·1 (5)	116·5 (4)
C(4a1)—C(4a)—C(4)	105·9 (4)	105·1 (3)
C(5)—C(4a)—C(4a1)	109·3 (4)	109·0 (3)
C(8a)—C(4a)—C(4a1)	112·2 (4)	112·3 (3)
C(8a1)—C(8a)—C(4a)	112·5 (4)	112·2 (3)
C(8a1)—C(8a)—C(1)	110·0 (4)	109·2 (3)
C(8a1)—C(8a)—C(8)	109·2 (4)	110·1 (3)



(I)



(II)

Fig. 1. Stereoscopic view of TTN (I) and THN (II).

Although the gross molecular conformations are similar for both molecules there are differences arising from the presence of two sp^3 C atoms, C(6) and C(7), in THN which are of sp^2 character in TTN. Thus the corresponding torsion angle C(5)—C(6)—C(7)—C(8) is −52·7 (5)° in THN and −1·0 (9)° in TTN. All intermolecular interactions correspond to van der Waals contacts.

The C(6)—C(7) bond length (1·290 Å) in the TTN molecule is shorter than the C(2)—C(3) bond distance (1·354 Å). The corresponding bond angles, C(5)—C(6)—C(7) and C(6)—C(7)—C(8), are larger than C(1)—C(2)—C(3) and C(2)—C(3)—C(4) (124·3 and 123·3 *vs* 120·8 and 120·3°). This inspection of bond lengths and angles reveals trends related to substitution as was already found for various substituted tetrahydronaphthoquinones (Phillips & Trotter, 1977) and tetrahydronaphthoquin-4α-ols (Greenhough & Trotter, 1981). Derivatives with Me groups at these positions have longer C=C bond length and smaller internal angles than those with H. This is consistent with expected changes of hybridization of the ring C atoms by substitution by electron-donating Me groups, accompanied by Me···Me steric interaction.

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Structure de l'Acétyl-2 *p*-Chlorophényl-8 Méthyl-4 Oxa-6 Triaza-2,3,7 Phospha-1 Bicyclo[3.3.0]octadiène-3,7, $C_{12}H_{11}ClN_3O_2P$. Premier Exemple d'Oxazaphospholodiazaphosphole

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Abstract. $M_r = 295·7$, monoclinic, $P2_1/n$, $a = 9·482$ (1), $b = 8·855$ (1), $c = 16·369$ (2) Å, $\beta = 101·3$ (3)°, $V = 1347·8$ (3) Å^3, $Z = 4$, $D_x = 1·457$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0·71069$ Å, $\mu = 0·039$ mm^{-1}, $F(000) = 588$, 293 K, $R = 0·047$ for 1260 observations. This compound is the first example of a primary dipolar 1,3-cycloadduct on P=C to be reported: the knowledge of its geometry allows discussion of the NMR results. The diazaphosphole and oxazaphosphole rings are in envelope conformations

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