

X-Ray Diffraction Study on (+)-1,3,3-Trimethylbicyclo[2.2.1]-heptan-2-one {(+)-Fenchone} (Z)-Oxime, Two Monochloro Derivatives and a Dehydrohalogenation Product[#]

Kari Rissanen,* Katri Laihia, Jorma Korvola and Erkki Kolehmainen

Department of Chemistry, University of Jyväskylä, SF-40100 Jyväskylä, Finland

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Structures of four (+)-1,3,3-trimethylbicyclo[2.2.1]heptan-2-one {(+)-fenchone} derivatives, (Z)-1,3,3-trimethylbicyclo[2.2.1]heptan-2-one oxime [1, (Z)-fenchone oxime], (Z)-1,3,3-trimethyl-*anti*-7-chlorobicyclo[2.2.1]heptan-2-one oxime [4, (Z)-*anti*-7-chlorofenchone oxime], (Z)-1,3-dimethyl-*exo*-3-chloromethylbicyclo[2.2.1]heptan-2-one oxime [5, (Z)-8-chlorofenchone oxime] and 6,6-dimethyl-3-oxa-4-azatricyclo[5.2.1.0^{1,5}]dec-4-ene (7), have been determined by X-ray diffraction. The compounds were obtained from the corresponding oxo compounds by treatment with hydroxylamine hydrochloride in alkaline ethanol. Compound 7 is a dehydrohalogenation product of 1-chloromethyl-3,3-dimethylbicyclo[2.2.1]heptan-2-one oxime (10-chlorofenchone oxime). Crystal data for the compounds: monoclinic, space group $P2_1$ (No. 2), $a = 6.219(2)$, $b = 11.250(1)$, $c = 14.475(1)$ Å, $\beta = 100.64(1)^\circ$, $V = 995.3(3)$ Å³ and $Z = 4$ (1), orthorhombic, space group $P2_12_12_1$ (No. 19), $a = 6.307(1)$, $b = 8.142(1)$, $c = 42.546(15)$ Å, $V = 2185(1)$ Å³ and $Z = 8$ (4), monoclinic, space group $P2_1$ (No. 2) $a = 6.231(2)$, $b = 22.357(10)$, $c = 7.848(3)$ Å, $\beta = 99.32(4)^\circ$, $V = 1079(1)$ Å³ and $Z = 4$ (5) and monoclinic, space group $P2_1$ (No. 2) $a = 6.152(4)$, $b = 10.278(8)$, $c = 7.764(7)$ Å, $\beta = 111.73(11)^\circ$, $V = 456(1)$ Å³ and $Z = 2$ (7). Full-matrix least-squares refinement of 217, 235, 235 and 108 parameters gave $R = 0.054, 0.056, 0.045$ and 0.041 for 1333, 1307, 1130 and 1163 reflections [$I > 3\sigma(I)$] for 1, 4, 5 and 7, respectively. The oximes 1, 4 and 5, which all have a Z C=N–OH group, form hydrogen-bond (–O–H \cdots N) connected dimers similarly to carboxylic acids. The N \cdots O distances in these dimers are: 2.774(6) and 2.817(5) Å (1), 2.772(8) and 2.806(8) Å (4) and 2.766(7) and 2.794(7) Å (5).

In two earlier papers we have reported both synthetic details and ¹H, ¹³C and ¹⁷O NMR spectroscopic parameters of (+)-1,3,3-trimethylbicyclo[2.2.1]heptan-2-one [(+)-fenchone], six monochloro derivatives¹ and the corresponding oxime derivatives.² The crystalline oximes were synthesized from the liquid monochlorofenchones in order to determine the stereochemistry of the chlorine substituent by X-ray diffraction. The X-ray data presented in this paper proved, however, unnecessary for the elucidation of the chlorine stereochemistry¹ but the stereochemistry of the oxime hydroxy [Z or E to C(3)] could not be determined unambiguously solely by NMR techniques.²

During the synthesis of the oxime derivatives (1–6, Fig. 1), Z and E isomers were originally formed. However, in the course of the reaction one of the isomers slowly disappeared. In the case of 1-chloromethyl-3,3-dimethylbicyclo[2.2.1]heptan-2-one (10-chlorofenchone) dehydrohalogenation occurred and a tricyclic derivative (7, Fig. 1) was formed instead of 10-chlorofenchone oxime.²

The conformationally rigid structure of fenchone, together with other compounds with bicyclo[2.2.1]heptane skeleton, is of great value in refining determining relationships involving structure-sensitive parameters, especially in NMR spectroscopy.^{1–9} These compounds have also been studied by X-ray diffraction^{10–12} and used as model compounds in conformational and stereochemical studies.¹³

In spite of the great efforts made to grow crystals suitable for X-ray diffraction analysis for all the compounds, only compounds 1, 4, 5 and 7 recrystallized sufficiently well. As a conclusion of our previous studies, we report here the crystal and molecular structure for (+)-(Z)-1,3,3-trimethylbicyclo[2.2.1]heptan-2-one oxime [1, (+)-(Z)-fenchone oxime], (+)-(Z)-1,3,3-trimethyl-*anti*-7-chlorobicyclo[2.2.1]heptan-2-one oxime [4, (+)-(Z)-*anti*-7-chlorofenchone oxime], (+)-(Z)-1,3-dimethyl-*exo*-3-chloromethylbicyclo[2.2.1]heptan-2-one oxime [5, (+)-(Z)-8-chlorofenchone oxime] and 6,6-dimethyl-3-oxa-4-azatricyclo[5.2.1.0^{1,5}]dec-4-ene (7).

*Part 3. For Part 2, see Ref. 2.

*To whom correspondence should be addressed.

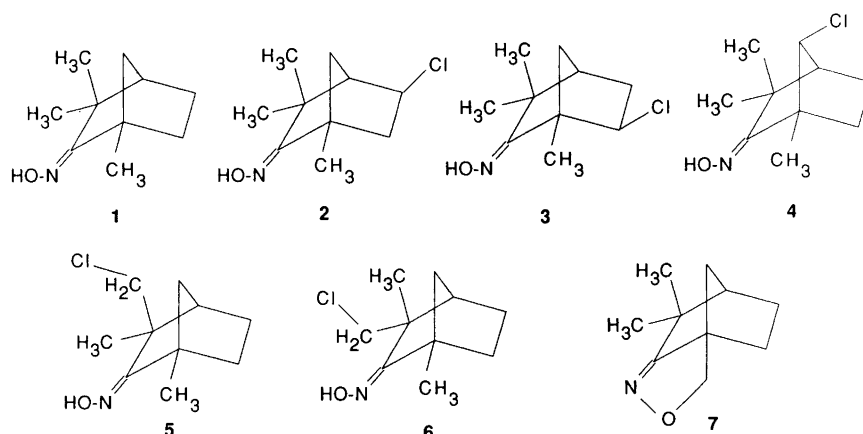


Fig. 1. Structures of (+)-fenchone oxime (1), five monochloro oximes (2–6) and a dehydrohalogenation product (7).

Table 1. Experimental crystallographic data for 1, 4, 5 and 7.

Compound	1	4	5	7
	$C_{10}H_{17}NO$	$C_{10}H_{16}ClNO$	$C_{10}H_{16}ClNO$	$C_{10}H_{15}NO$
M_r	167.25	201.70	201.70	165.24
$a/\text{\AA}$	6.219(2)	6.307(1)	6.231(22)	6.152(4)
$b/\text{\AA}$	11.250(1)	8.142(1)	22.357(10)	10.278(8)
$c/\text{\AA}$	14.475(1)	42.546(15)	7.848(3)	7.764(7)
$\alpha/^\circ$	90	90	90	90
$\beta/^\circ$	100.64(1)	90	99.32(4)	111.73(11)
$\gamma/^\circ$	90	90	90	90
$V/\text{\AA}^3$	995.3(3)	2185(1)	1079(1)	456(1)
Z	4	8	4	2
$d_{\text{calc}}/\text{Mg m}^{-3}$	1.116	1.226	1.242	1.203
μ/mm^{-1}	0.07	0.31	0.32	0.07
$\lambda/\text{Mo } K_\alpha$	0.71073	0.71073	0.71073	0.71073
$F(000)$	368	864	432	180
Space group	$P2_1$ (No. 4)	$P2_12_12_1$ (No. 19)	$P2_1$ (No. 4)	$P2_1$ (No. 4)
T/K	296 ± 1	296 ± 1	296 ± 1	296 ± 1
Crystal size/mm	$0.20 \times 0.18 \times 0.15$	$0.15 \times 0.17 \times 0.22$	$0.16 \times 0.23 \times 0.24$	$0.25 \times 0.15 \times 0.23$
Refl. for latt. meas.	25	25	25	25
θ range for latt. meas./ $^\circ$	6–12	15–19	15–19	4–12
Scan method	$\omega/2\theta$	$\omega/2\theta$	$\omega/2\theta$	$\omega/2\theta$
Scan speed/ $^\circ \text{ min}^{-1}$	1–17	1–17	1–17	1–17
Scan width (ω)/ $^\circ$	$0.48 + 0.34 \tan\theta$	$0.60 + 0.34 \tan\theta$	$1.00 + 0.34 \tan\theta$	$1.20 + 0.34 \tan\theta$
θ range/ $^\circ$	2–25	2–30	2–25	2–30
h range	0→7	0→8	0→7	0→8
k range	0→13	0→11	0→26	0→14
l range	–17→16	0→59	–9→19	–10→10
Variation of std. refl.	None	None	None	None
Refl. measured	1847	3702	1966	1398
Number of unique refl.	1847	3702	1966	1398
Condition of obs. refl.	$I > 3.0\sigma(I)$	$I > 3.0\sigma(I)$	$I > 3.0\sigma(I)$	$I > 3.0\sigma(I)$
Refl. used in refinement	1333	1307	1130	1163
Max. shift/error	< 0.01	0.01	0.04	< 0.01
No. of param.	217	235	236	108
Max./min. in final $\Delta\rho/e \text{\AA}^{-3}$	0.29(3)/–0.14(3)	0.30(4)/–0.23(4)	0.37(4)/–0.20(4)	0.11(3)/–0.06(3)
S	0.65	1.60	1.17	0.31
R	0.054	0.056	0.045	0.041
R_w	0.052	0.082	0.067	0.034
$w = 1/[\sigma^2 F_0 + (a F_0)^2]$	$a = 0.03$	$a = 0.05$	$a = 0.05$	$a = 0.001$

Experimental

Preparation of the compounds. The crystalline oxime derivatives were synthesized by refluxing fenchone or mono-chlorofenchones¹ with sodium acetate and hydroxylamine hydrochloride in 99 % ethanol under dry conditions for 52 h. The oximes **1**, **4** and **5** and the tricyclic derivative **7** were recrystallized from light petroleum–ethanol solution (1:1 to 1:10).²

Crystal structure analysis of 1, 4, 5 and 7. The crystal data and conditions for the data collections are given in Table 1.* The lattice parameters were determined by measuring 25 reflections using Mo K_α (λ = 0.71073 Å) radiation at room temperature (296 ± 1 K). Intensity data were collected on an Enraf–Nonius CAD4 diffractometer. The intensity data were corrected for Lorentz and polarization effects but not for extinction. Empirical absorption corrections were made according to Walker and Stuart¹⁴ for the data sets, the maximum and minimum correction coefficients being 0.873 and 1.266 for **1**, 0.923 and 1.201 for **4**, 0.798 and 1.311 for **5** and 0.932 and 1.156 for **7**. The structures were solved by direct methods using the MULTAN 11/82 program.¹⁵ The final refinements were carried out by full-matrix least-squares using the SDP-plus

Table 2. Fractional coordinates and equivalent isotropic temperature factors^a with e.s.d.s in parentheses for **1**.

Atom	x	y	z	B _{eq} /Å ²
O(1A)	0.1656(7)	0.426	0.3073(3)	5.6(1)
O(1B)	0.3290(6)	0.2033(4)	0.1938(3)	4.9(1)
N(1A)	0.0713(7)	0.4003(4)	0.2115(3)	4.2(1)
N(1B)	0.4267(7)	0.2257(4)	0.2885(3)	4.2(1)
C(1A)	-0.1770(8)	0.4632(5)	0.0718(4)	4.0(1)
C(1B)	0.7016(9)	0.1634(6)	0.4211(4)	4.7(1)
C(2A)	-0.0651(8)	0.4764(4)	0.1736(4)	3.5(1)
C(2B)	0.5805(8)	0.1520(5)	0.3201(4)	3.6(1)
C(3B)	0.6711(9)	0.0464(5)	0.2745(4)	4.4(1)
C(3A)	-0.1431(9)	0.5918(5)	0.2118(4)	4.5(1)
C(4B)	0.855(1)	0.0069(6)	0.3590(4)	6.0(2)
C(4A)	-0.3034(9)	0.6355(6)	0.1212(4)	5.0(1)
C(5A)	-0.5093(9)	0.5582(7)	0.1011(5)	6.0(2)
C(5B)	0.748(1)	-0.0518(7)	0.4332(5)	7.3(2)
C(6A)	-0.4210(9)	0.4375(6)	0.0726(5)	5.7(2)
C(6B)	0.632(1)	0.0542(7)	0.4724(4)	6.3(2)
C(7A)	-0.1863(9)	0.5952(5)	0.0428(4)	4.6(1)
C(7B)	0.933(1)	0.1267(7)	0.4048(5)	6.6(2)
C(8A)	0.049(1)	0.6811(6)	0.2378(5)	6.0(2)
C(8B)	0.498(1)	-0.0477(6)	0.2408(5)	7.0(2)
C(9A)	-0.259(1)	0.5704(7)	0.2958(4)	6.4(2)
C(9B)	0.784(1)	0.0898(8)	0.1923(4)	7.5(2)
C(10A)	-0.069(1)	0.3754(6)	0.0149(4)	5.7(2)
C(10B)	0.681(1)	0.2811(7)	0.4678(5)	7.9(2)

$$^a B_{eq} = (4/3) \sum_i \sum_j \beta_{ij} a_i \cdot a_j$$

*Lists of structure factors, H-atom coordinates and anisotropic temperature factors may be obtained from one of the authors (K.R.) on request.

Table 3. Fractional coordinates and equivalent isotropic temperature factors^a with e.s.d.s in parentheses for **4**.

Atom	x	y	z	B _{eq} /Å ²
Cl(A)	0.9641(4)	0.8700(2)	0.97463(4)	5.71(4)
Cl(B)	2.0456(4)	-0.0868(3)	0.80508(7)	7.48(6)
O(A)	1.252(1)	2.2688(6)	0.8971(1)	5.7(1)
O(B)	1.511(1)	0.5091(6)	0.8491(1)	5.6(1)
N(A)	1.2217(9)	0.4411(7)	0.8974(1)	4.0(1)
N(B)	1.529(1)	0.3342(7)	0.8482(1)	4.3(1)
C(1A)	1.048(1)	0.6733(8)	0.9223(1)	3.7(1)
C(1B)	1.698(1)	0.1011(8)	0.8231(1)	3.6(1)
C(2A)	1.101(1)	0.4913(8)	0.9195(2)	3.6(1)
C(2B)	1.665(1)	0.2824(8)	0.8278(1)	3.5(1)
C(3B)	1.805(1)	0.3758(8)	0.8054(2)	3.9(1)
C(3A)	0.991(1)	0.3958(8)	0.9452(1)	3.7(1)
C(4A)	0.875(1)	0.5415(8)	0.9628(2)	3.9(1)
C(4B)	1.915(1)	0.2291(8)	0.7879(2)	4.0(1)
C(5A)	0.694(1)	0.608(1)	0.9432(2)	5.1(2)
C(5B)	1.757(1)	0.140(1)	0.7670(2)	5.6(2)
C(6B)	1.601(1)	0.060(1)	0.7906(2)	5.2(2)
C(6A)	0.806(1)	0.688(1)	0.9147(2)	4.8(2)
C(7B)	1.936(1)	0.1085(8)	0.8160(2)	4.4(1)
C(7A)	1.045(1)	0.6745(7)	0.9588(1)	3.8(1)
C(8A)	1.156(1)	0.3127(9)	0.9675(2)	5.1(2)
C(8B)	1.970(1)	0.4783(9)	0.8230(2)	5.0(2)
C(9A)	0.838(1)	0.265(1)	0.9323(2)	5.5(2)
C(9B)	1.683(2)	0.4883(9)	0.7829(2)	5.9(2)
C(10A)	1.187(2)	0.7895(9)	0.9059(2)	5.3(2)
C(10B)	1.621(2)	-0.0086(9)	0.8501(2)	5.8(2)

$$^a B_{eq} = (4/3) \sum_i \sum_j \beta_{ij} a_i \cdot a_j$$

Table 4. Fractional coordinates and equivalent isotropic temperature factors^a with e.s.d.s in parentheses for **5**.

Atom	x	y	z	B _{eq} /Å ²
Cl(A)	1.5057(3)	1.442	1.1577(3)	8.47(5)
Cl(B)	0.3744(4)	1.0688(1)	0.5598(3)	7.07(5)
O(1A)	0.9001(8)	1.3377(2)	0.9765(6)	6.0(1)
O(1B)	0.6068(8)	1.2522(2)	0.6984(6)	6.3(1)
N(1A)	0.9183(8)	1.3409(2)	0.7950(6)	4.4(1)
N(1B)	0.6103(8)	1.2454(2)	0.8802(6)	4.5(1)
C(1A)	1.094(1)	1.3917(3)	0.5798(7)	4.6(1)
C(1B)	0.481(1)	1.1869(3)	1.1035(8)	4.6(1)
C(2A)	1.0474(9)	1.3813(3)	0.7580(8)	4.0(1)
C(2B)	0.4969(9)	1.2019(3)	0.9208(8)	4.2(1)
C(3A)	1.1789(9)	1.4258(3)	0.8825(7)	4.2(1)
C(3B)	0.3675(9)	1.1556(3)	0.8035(7)	4.1(1)
C(4A)	1.295(1)	1.4604(3)	0.7492(9)	4.7(1)
C(4B)	0.288(1)	1.1157(3)	0.9433(8)	4.8(1)
C(5A)	1.132(1)	1.4987(3)	0.631(1)	6.3(2)
C(5B)	0.116(1)	1.1479(4)	1.027(1)	6.1(2)
C(6A)	0.987(1)	1.4524(3)	0.5249(9)	5.7(1)
C(6B)	0.241(1)	1.2002(3)	1.127(1)	6.0(2)
C(7A)	1.335(1)	1.4098(3)	0.6227(8)	5.1(1)
C(7B)	0.475(1)	1.1186(3)	1.0909(8)	4.9(1)
C(8A)	1.344(1)	1.3927(3)	1.0107(8)	5.4(1)
C(8B)	0.517(1)	1.1211(3)	0.7068(8)	5.2(1)
C(9A)	1.033(1)	1.4658(3)	0.974(1)	6.3(2)
C(9B)	0.181(1)	1.1843(4)	0.675(1)	6.7(2)
C(10A)	1.034(2)	1.3414(3)	0.452(1)	7.9(2)
C(10B)	0.647(1)	1.2166(4)	1.241(1)	6.9(2)

$$^a B_{eq} = (4/3) \sum_i \sum_j \beta_{ij} a_i \cdot a_j$$

Table 5. Fractional coordinates and equivalent isotropic temperature factors^a with e.s.d.s in parentheses for **7**.

Atom	x	y	z	$B_{\text{eq}}/\text{\AA}^2$
O(1)	0.3428(4)	0.604	-0.1040(2)	5.38(6)
N(1)	0.3791(4)	0.5535(3)	0.0778(3)	4.61(7)
C(1)	0.1711(4)	0.7492(4)	0.0435(3)	3.32(7)
C(2)	0.2822(4)	0.6323(3)	0.1526(3)	3.33(7)
C(3)	0.2787(4)	0.6398(3)	0.3452(3)	3.55(7)
C(4)	0.1607(5)	0.7765(4)	0.3270(4)	3.89(8)
C(5)	-0.0994(5)	0.7693(4)	0.2017(4)	4.96(9)
C(6)	-0.0939(4)	0.7417(4)	0.0071(4)	4.60(8)
C(7)	0.2559(5)	0.8502(4)	0.1973(3)	4.24(8)
C(8)	0.5276(5)	0.6426(5)	0.4941(4)	5.50(9)
C(9)	0.1455(5)	0.5276(4)	0.3899(4)	5.41(9)
C(10)	0.2508(5)	0.7358(4)	-0.1178(4)	4.83(9)

$$^a B_{\text{eq}} = (4/3) \sum_i \sum_j \beta_{ij} \mathbf{a}_i \cdot \mathbf{a}_j$$

program package,¹⁶ anisotropically for all non H-atoms. The hydrogen atoms were calculated to their idealized positions (C–H distance 1.03 Å) and refined isotropically as riding atoms with a fixed isotropic temperature factor ($B = 5.0 \text{ \AA}^2$). The atomic scattering factors were taken from Ref. 17. The final coordinates are given in Tables 2–5. In addition to the programs quoted the PLUTO¹⁸ program was used. The calculations were performed on a micro-VAX II computer at the Department of Chemistry, University of Jyväskylä.

Results and discussion

The bond distances and angles are given in Tables 6 and 7. A view, illustrating the dimer formation and the hydrogen bonding in oximes **1**, **4** and **5**, is presented in Fig. 2 (oxime **4** with labelling scheme). A view of the molecules **1**, **4**, **5** and **7** is shown in Fig. 3 and the packing schemes in Figs. 4–7, respectively.

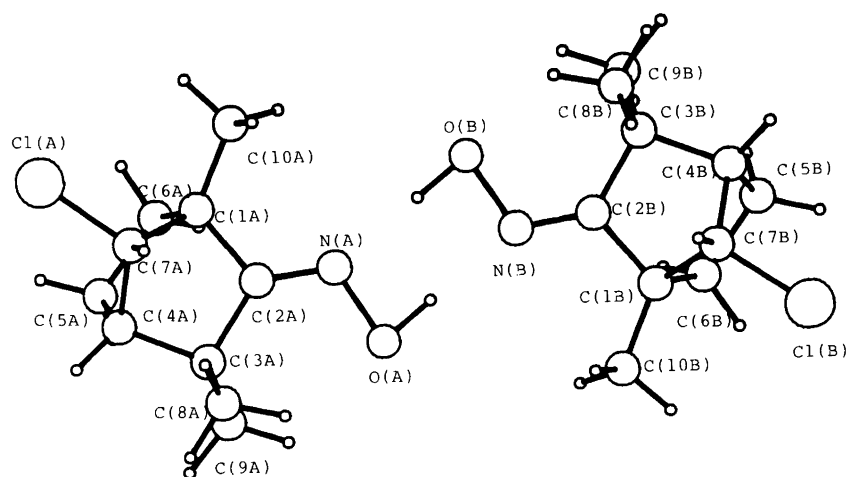


Fig. 2. PLUTO plot showing dimer formation and hydrogen bonding with the numbering scheme for **4**.

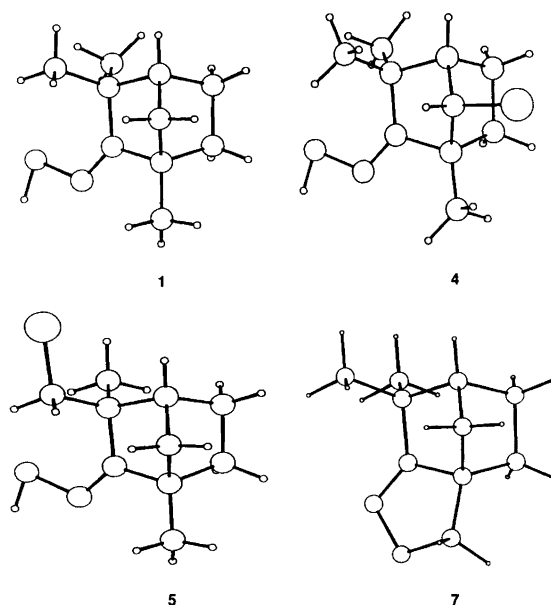


Fig. 3. PLUTO plots for the oximes **1**, **4**, **5** and the cyclic derivative **7**.

The chlorine substituent does not induce changes within the rigid bicyclo[2.2.1]heptane skeleton in the oximes **4** and **5** when compared with the non-halogenated oxime **1** (Tables 6 and 7). These observations are in accordance with the ¹H and ¹³C NMR parameters^{1,2} and also with the X-ray diffraction studies on other bicyclo[2.2.1]heptane derivatives.^{10–12,19} The Cl–C(sp³) and the mean C(sp³)–C(sp³) and C(sp³)–C(sp²) distances agree well with the values presented by Trotter²⁰ and Rettig and Trotter¹³ [1.75–1.85 Å for Cl–C(sp³) and 1.54 and 1.52 Å for the C–C bonds, respectively]. The C=N distances are 0.06–0.08 Å longer than the C=O distance (1.21–1.23 Å) in fenchone and camphor derivatives^{10–12} and are in accordance with the

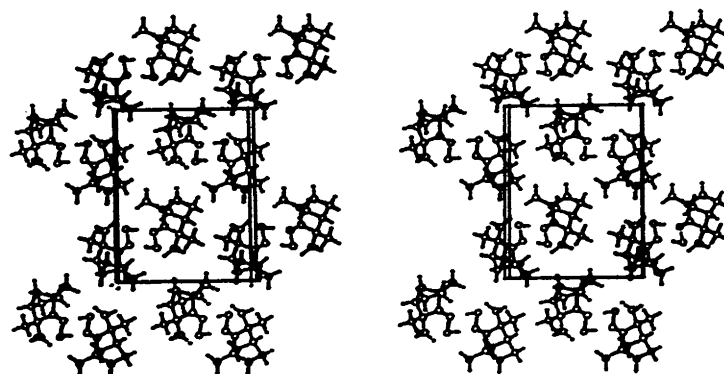


Fig. 4. Stereoscopic PLUTO plot for 1. The *c* axis is vertical and *b* axis horizontal.

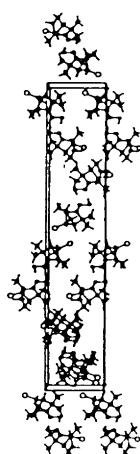
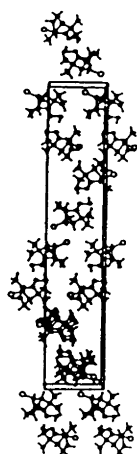


Fig. 5. Stereoscopic PLUTO plot for 4. The *c* axis is vertical and *b* axis horizontal.

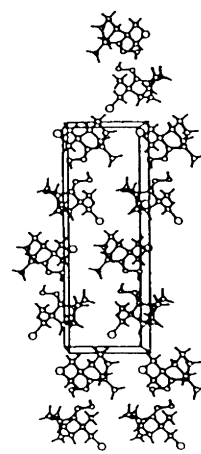
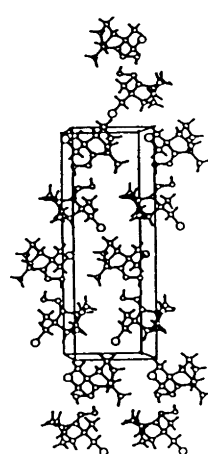


Fig. 6. Stereoscopic PLUTO plot for 5. The *b* axis is vertical and *c* axis horizontal.

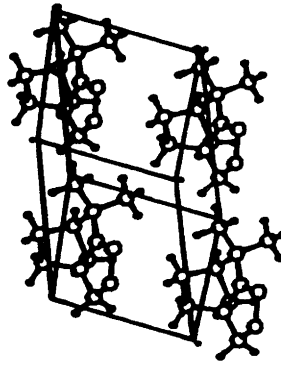
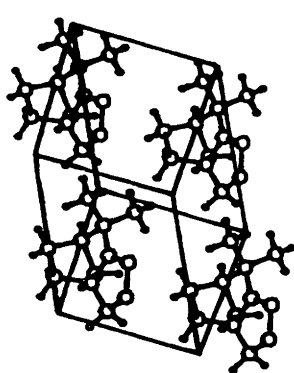


Fig. 7. Stereoscopic PLUTO plot for 7. The *b* axis is vertical and *c* axis horizontal.

Table 6. Bond distances (Å) for **1**, **4**, **5** and **7** with e.s.d.s. in parentheses.

	1 (A)	1 (B)	4 (A)	4 (B)	5 (A)	5 (B)	7
O(1)–N(1)	1.432(5)	1.415(5)	1.416(8)	1.429(7)	1.449(7)	1.431(7)	1.443(3)
O(1)–C(10)	–	–	–	–	–	–	1.452(4)
N(1)–C(2)	1.257(6)	1.285(7)	1.276(9)	1.290(9)	1.273(8)	1.272(8)	1.267(4)
C(1)–C(2)	1.517(7)	1.521(7)	1.524(9)	1.504(9)	1.492(9)	1.492(9)	1.483(4)
C(1)–C(6)	1.546(8)	1.539(9)	1.565(11)	1.547(9)	1.543(9)	1.564(9)	1.550(4)
C(1)–C(7)	1.542(8)	1.558(9)	1.555(8)	1.531(11)	1.538(9)	1.531(9)	1.521(4)
C(1)–C(10)	1.519(9)	1.503(10)	1.464(11)	1.534(10)	1.515(9)	1.523(9)	1.511(4)
C(2)–C(3)	1.525(8)	1.517(8)	1.513(9)	1.505(9)	1.536(8)	1.526(8)	1.505(4)
C(3)–C(4)	1.573(7)	1.577(8)	1.580(9)	1.569(9)	1.568(9)	1.558(9)	1.563(5)
C(3)–C(8)	1.555(8)	1.523(9)	1.563(10)	1.528(11)	1.512(8)	1.506(9)	1.540(3)
C(3)–C(9)	1.541(9)	1.567(9)	1.539(11)	1.534(11)	1.532(10)	1.548(9)	1.528(5)
C(4)–C(5)	1.531(9)	1.514(10)	1.511(10)	1.524(11)	1.524(9)	1.524(10)	1.536(3)
C(4)–C(7)	1.525(9)	1.542(10)	1.535(10)	1.553(9)	1.552(9)	1.508(8)	1.538(5)
C(5)–C(6)	1.552(10)	1.560(10)	1.546(11)	1.548(11)	1.531(10)	1.544(10)	1.550(4)
Cl–C(7)	–	–	1.802(7)	1.797(7)	–	–	–
Cl–C(8)	–	–	–	–	1.790(7)	1.778(7)	–

Table 7. Bond angles (°) for **1**, **4**, **5** and **7** with e.s.d.s. in parentheses.

	1 (A)	1 (B)	4 (A)	4 (B)	5 (A)	5 (B)	7
O(1)–N(1)–C(2)	114.1(4)	112.8(4)	113.8(5)	113.3(5)	114.3(4)	114.3(5)	106.7(2)
O(1)–C(10)–C(1)	–	–	–	–	–	–	105.1(3)
N(1)–O(1)–C(10)	–	–	–	–	–	–	108.9(2)
C(2)–C(1)–C(6)	106.6(5)	105.3(5)	105.8(6)	106.1(5)	104.9(5)	106.5(5)	107.2(3)
C(2)–C(1)–C(7)	99.1(4)	98.0(4)	95.0(5)	96.9(5)	99.6(4)	99.6(5)	98.8(2)
C(6)–C(1)–C(7)	101.2(5)	102.3(5)	101.1(5)	102.7(5)	101.0(5)	100.6(5)	102.1(3)
C(2)–C(1)–C(10)	114.9(5)	116.0(5)	117.4(6)	115.3(6)	116.3(6)	116.0(6)	100.2(3)
C(6)–C(1)–C(10)	114.5(5)	115.6(5)	115.7(6)	115.0(6)	114.8(5)	113.0(6)	119.1(2)
C(7)–C(1)–C(10)	118.5(5)	117.3(5)	118.7(6)	118.4(6)	117.9(7)	119.1(5)	126.2(3)
N(1)–C(2)–C(1)	120.6(5)	119.5(5)	120.0(6)	120.1(6)	123.3(5)	122.6(5)	116.8(2)
N(1)–C(2)–C(3)	131.0(5)	131.5(4)	130.0(6)	130.6(6)	127.3(5)	128.9(5)	132.1(3)
C(1)–C(2)–C(3)	108.4(4)	109.4(4)	110.0(5)	109.3(5)	109.3(5)	108.4(5)	110.6(3)
C(2)–C(3)–C(4)	99.1(4)	99.1(4)	99.7(5)	100.1(5)	98.7(5)	99.3(4)	97.7(2)
C(2)–C(3)–C(8)	110.8(5)	112.8(5)	110.6(6)	111.4(5)	109.9(5)	110.0(5)	111.8(2)
C(2)–C(3)–C(9)	112.3(5)	108.3(5)	112.7(5)	113.6(7)	112.4(5)	112.4(5)	113.2(3)
C(4)–C(3)–C(8)	109.9(5)	114.9(5)	110.3(5)	110.4(6)	110.4(5)	110.8(5)	110.5(3)
C(4)–C(3)–C(9)	113.0(5)	108.3(5)	113.5(6)	112.3(5)	113.4(5)	114.0(5)	115.4(3)
C(8)–C(3)–C(9)	111.1(5)	111.2(5)	109.6(6)	108.8(6)	111.4(5)	110.0(5)	108.1(3)
C(3)–C(4)–C(5)	111.5(5)	108.8(5)	110.9(5)	110.6(6)	110.4(5)	111.0(5)	110.7(3)
C(3)–C(4)–C(7)	102.2(4)	102.3(4)	98.9(5)	98.7(5)	101.9(5)	102.7(5)	103.0(3)
C(5)–C(4)–C(7)	100.8(5)	102.8(5)	102.4(6)	101.7(6)	100.5(5)	99.2(5)	99.7(2)
C(4)–C(5)–C(6)	102.9(5)	102.6(6)	103.8(6)	103.6(5)	103.1(5)	104.2(5)	103.5(2)
C(1)–C(6)–C(5)	103.6(5)	104.1(5)	104.6(6)	103.9(6)	104.8(5)	102.1(6)	102.3(2)
C(1)–C(7)–C(4)	94.7(4)	94.0(5)	96.5(5)	95.4(5)	94.7(5)	95.7(5)	94.3(3)
Cl–C(7)–C(4)	–	–	112.4(4)	113.2(5)	–	–	–
Cl–C(7)–C(1)	–	–	112.5(5)	113.0(5)	–	–	–
Cl–C(8)–C(3)	–	–	–	–	112.1(5)	112.3(5)	–

C=N distances found in various cyclic or bicyclic oximes.^{19,21–26} The C(1)–C(7)–C(4) bridge angle values are within two degrees (94.5–96.5°) and comparable to the values in other bicyclo[2.2.1]heptanes.^{10–12,19} In the dehydrohalogenation product of 10-chlorofenchone oxime, 6,6-dimethyl-3-oxa-4-azatricyclo[5.2.1.0^{1,5}]dec-4-ene (**7**), the bicyclo[2.2.1]heptane moiety shows great similarity with the oximes **1**, **4** and **5**, but the formation of an O–C bond and the closing of the five-membered ring due to the re-

moval of HCl induces extra strain in the molecule. This can be observed as a large decrease in the O(1)–N(1)–C(2), C(2)–C(1)–C(10) and N(1)–C(2)–C(1) angle values: from ca. 113 to 106.7(2), ca. 115.5 to 100.2(3) and ca. 120.5 to 116.8(2)°, respectively. Also, molecular mechanics calculations² lend further support for the increased strain by giving a total energy that is ca. 40 kJ mol^{–1} higher than that of fenchone oxime (**1**). MM calculations also indicate why only one tricyclic derivative is formed; corresponding tricy-

clic derivatives might also be expected to be formed from the 8- and 9-chlorofenchone oximes (**5** and **6**). The calculations showed that dehydrochlorination products of **5** and **6** would still be energetically ca. 46 and 38 kJ mol⁻¹ more strained than **7**.

The *Z* or *E* stereochemistry of the oximes could not be resolved by the NMR techniques and MM calculations used.² The theoretical calculations indicated the difference between *Z* and *E* forms to be less than 4 kJ mol⁻¹ and the ¹⁷O NMR chemical shifts were not structure dependent as was the case for fenchone and six monochlorofenchones.¹ The results obtained now for the crystalline oximes (Fig. 3) clearly show that the oxime hydroxy group is *Z* to C(3) for **1**, **4** and **5**. Based on the NMR data² it is probable that the unrecrystallizable oximes **2**, **3** and **6** are also in *Z* form. The formation of **7** is possible only through dehydrochlorination of the (*E*)-10-chlorofenchone oxime. In the crystalline state the oximes **1**, **4** and **5** form dimers through the hydrogen bonds between the oxime groups in adjacent molecules in a manner similar to carboxylic acids (Fig. 2). The N(A)⋯O(B) and N(B)⋯O(A) distances in these dimers are 2.774(6) and 2.817(5) (**1**), 2.772(8) and 2.806(8) (**4**) and 2.766(7) and 2.794(7) Å (**5**), indicating quite strong hydrogen bonding. The values agree well with the distances found in similar oximes,^{19,21-26} where the distances range from 2.72(1) to 2.864(9) Å, independent on the *Z* or *E* configuration of the oxime group. The broad ¹⁷O NMR signals² for the oximes **1-6** appeared at a fairly constant value of 180-185 ppm (from external D₂O reference at 40°C), while the tricyclic derivative **7** without an oxime group gave a well resolved signal at 235.2 ppm, indicating that, for the oximes **1-6**, dimer formation is also preferred in the liquid state.

The crystal lattices (Figs. 4-7) are composed of loosely packed hydrogen-bonded dimers (**1**, **4** and **5**) or molecules (**7**). The densities are low, especially for the chlorine-containing oximes **4** and **5**, but still comparable to similar dimer systems.^{19,21,22} Dimer formation reduces the possibility of forming even weak hydrogen bonds between the adjacent dimers, thus leaving only the weakly attracting van der Waals forces between the molecules. Owing to the packing there are no intermolecular contacts shorter than the sum of van der Waals' radii, the minimum contact distance being Cl(A)⋯Cl(B) (2-x, y+1/2, 2-z), 3.595(3) Å, for the oxime **5**.

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