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Spirocyclohexane Oxazines, Thiazines and Selenazines. Crystal Structures and NMR Comparative Study

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Abstract

The crystal structures of cyclohexanespiro-2-{4-phenyl-5-aza-3-oxabicyclo[4.4.0]deca-1(6),4-diene} (I) and the corresponding spirothiazine (II) were solved by direct methods using three-dimensional X-ray diffraction data. Compound (I), $C_{19}H_{23}NO$, $M_r = 281.4$, monoclinic, space group $P2_1/c$, $a = 15.157$ (9), $b = 10.584$ (3), $c = 9.745$ (3) Å, $\beta = 96.38°$, $V = 1553.6$ Å^3, $Z = 4$, $D_x = 1.20$ Mg m^{-3}, Mo $K\bar{\alpha}$, $\lambda = 0.7107$ Å, $\mu = 0.39$ mm^{-1}, $F(000) = 608$, $T = 293$ K, $R = 0.058$ for 1782 reflections with $I > 3\sigma(I)$. Compound (II), $C_{19}H_{23}NS$, $M_r = 293.5$, monoclinic, space group $P2_1/a$, $a = 9.901$ (3), $b = 19.074$ (9), $c = 9.411$ (3) Å, $\beta = 114.10°$, $V = 1622.3$ Å^3, $Z = 4$, $D_x = 1.20$ Mg m^{-3}, Mo $K\bar{\alpha}$, $\lambda = 0.7107$ Å, $\mu =$

1.54 mm^{-1}, $F(000) = 640$, $T = 293$ K, $R = 0.052$ for 2448 reflections with $I > 3\sigma(I)$. H atoms were found on a difference map and some were readjusted to their theoretical value. A least-squares analysis of the rigid-body motion of the molecules shows that the part of the spirothiazine compound (II) excluding the benzene ring is more rigid than the similar part of molecule (I). However, the torsional oscillations around the C3—C16 bond are more important in molecule (II) [r.m.s. $5.02(1.5)$ for (II) and $4.09(1.1)$ for (I)]. The ^{1}H and ^{13}C NMR spectra of compounds (I) and (II) and their selena homolog in solution are assigned by one- and two-dimensional techniques. The conformations of the molecules in solution are almost identical and very similar to those obtained in the solid state.

Introduction

Oxazines, thiazines and selenazines belong to different classes of compounds with chemical, pharmaceutical and industrial applications which have been amply demonstrated in the literature (Schmidt, 1972; Le Perchec, 1986; Sainsbury, 1984). It is also well known that the methodologies for the elaboration of quarternary carbon centers have become increasingly sophisticated (Martin, 1980) and when the molecular architecture includes a spiro carbon center, the synthetic challenge is particularly demanding (Krapcho, 1976).

For these different reasons, it seemed interesting to carry out a detailed comparative study of the structures of the oxazine (I), thiazine (II) and selenazine (III), which possess a spiroheterocyclic framework.
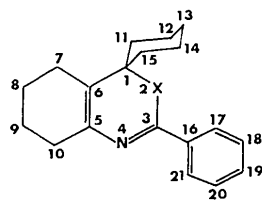
(I) $X = O$
(II) $X = S$
(III) $X = Se$

Compounds (I), (II) and (III) have been studied by NMR spectroscopy; only compounds (I) and (II), which gave suitable crystals, have been investigated by X-ray diffraction.

Experimental

Synthesis and crystallization

Cyclohexanespiro-2-{4-phenyl-5-aza-3-oxabicyclo-[4.4.0]deca-1(6),4-diene} (I) was prepared by condensation under acidic conditions of benzamide (IV)

with 2-(1-cyclohexenyl)cyclohexanone (VII), which was produced by aldol dimerization of cyclohexanone.

(IV) $X = O$
(V) $X = S$
(VI) $X = Se$

(VII)

(VIII)

(I) $X = O$
(II) $X = S$
(III) $X = Se$
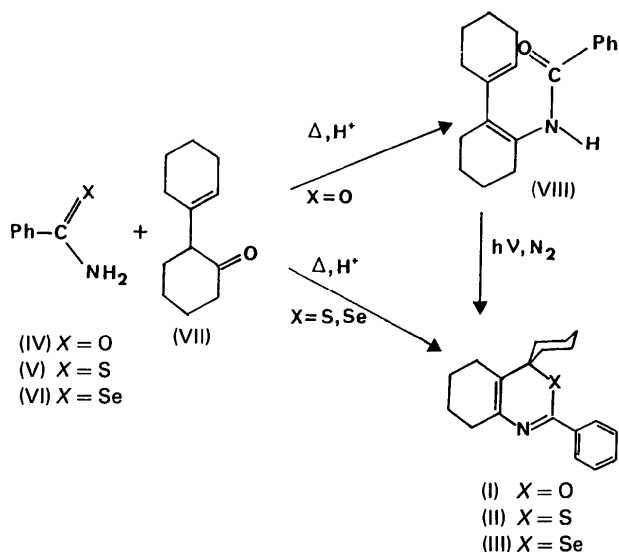
The annelation of the primary product (VIII) was achieved photochemically (Bochu, Couture & Lablache-Combier, 1986), by irradiating a carefully degassed solution of (VIII) in hexane ($5 \times 10^{-3}M$, 2537 Å, 2 h).

The corresponding spirothiazine (II) and selenazine (III), were readily accessible by direct condensation of the carboxamides (V) and (VI) (Cohen, 1978) with the bicyclic ketone (VII).

Compounds (I) and (II) were obtained as white crystals after recrystallization in a toluene–hexane mixture [m.p. 370–371 K for (I) and 362–363 K for (II)].

NMR

The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AM 400 WB spectrometer at 298 K using 5 mm o.d. sample tubes containing solutions of the samples in C_6D_6 or in $CDCl_3$. Chemical-shift references were tetramethylsilane (Me$_4$Si) or the appropriate solvent relative to Me$_4$Si. Typical ^{1}H acquisition parameters were sweep width 4032 Hz and 25° flip angle corresponding to 3 μs. The ^{13}C spectra were recorded at 100.62 MHz with Waltz proton decoupling (decoupler power of 0.6 W). Typical acquisition parameters were sweep width 23 809 Hz, 30° flip angle corresponding to 2 μs, pulse repetition rate 3.38 s and $NS = 400$ transients. Spectral editing was performed using the standard DEPT sequence of the Bruker micro program library (Bendall, Doddrell, Pegg & Hull, 1983); the 90° decoupler pulse was 10.6 μs.

The two-dimensional experiments were performed by application of standard micro programs (Morris, 1986;

Table 1. *Fractional atomic coordinates* ($\times 10^4$) *and equivalent isotropic temperature factors* ($\text{Å}^2 \times 10^2$) *with e.s.d.'s in parentheses*

$$U_{eq} = \tfrac{1}{3}\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i . \mathbf{a}_j.$$

	(I)				(II)			
A†	x	y	z	U_{eq}	x	y	z	U_{eq}
A†	7309 (1)	825 (2)	7019 (2)	37 (3)	5369 (1)	1055 (1)	5613 (1)	43 (1)
N	8596 (2)	−166 (3)	6432 (3)	37 (3)	3810 (3)	333 (1)	6893 (3)	44 (3)
C1	7738 (2)	1194 (3)	8400 (3)	36 (4)	6809 (3)	866 (2)	7562 (4)	36 (3)
C3	7759 (2)	6 (3)	6279 (3)	36 (4)	3798 (3)	802 (2)	5927 (4)	36 (3)
C5	9095 (2)	612 (3)	7414 (3)	36 (4)	5099 (3)	−57 (2)	7744 (4)	41 (3)
C6	8726 (2)	1299 (3)	8349 (3)	36 (4)	6484 (3)	151 (2)	8075 (4)	40 (3)
C7	9261 (2)	2112 (4)	9410 (4)	40 (4)	7805 (4)	−278 (2)	9121 (4)	54 (4)
C8	10253 (3)	1836 (4)	9493 (4)	43 (5)	7385 (4)	−853 (2)	10012 (5)	73 (5)
C9	10553 (2)	1695 (4)	8067 (4)	47 (5)	6032 (4)	−1233 (2)	8972 (5)	73 (5)
C10	10073 (2)	603 (4)	7280 (4)	41 (4)	4721 (4)	−741 (2)	8301 (4)	55 (4)
C11	7297 (3)	2445 (4)	8691 (4)	46 (5)	8274 (4)	887 (2)	7349 (4)	51 (4)
C12	6299 (3)	2312 (4)	8749 (4)	57 (6)	8644 (4)	1626 (2)	6942 (5)	58 (4)
C13	6105 (3)	1332 (5)	9820 (4)	69 (7)	8671 (4)	2161 (2)	8167 (5)	56 (5)
C14	6513 (3)	59 (5)	9516 (4)	69 (6)	7212 (4)	2162 (2)	8345 (5)	53 (4)
C15	7513 (3)	172 (4)	9427 (4)	52 (5)	6824 (3)	1432 (2)	8737 (4)	42 (4)
C16	7171 (2)	−640 (3)	5188 (3)	34 (4)	2389 (4)	1153 (2)	4921 (4)	40 (3)
C17	6268 (2)	−723 (4)	5237 (4)	44 (4)	2351 (4)	1805 (2)	4238 (5)	60 (5)
C18	5731 (2)	−1328 (4)	4181 (4)	47 (5)	1006 (5)	2105 (2)	3298 (6)	79 (6)
C19	6103 (3)	−1852 (4)	3083 (4)	43 (5)	−302 (5)	1769 (3)	3015 (5)	73 (6)
C20	7007 (3)	−1778 (4)	3028 (4)	48 (5)	−287 (4)	1119 (3)	3674 (6)	72 (6)
C21	7544 (2)	−1176 (4)	4080 (4)	43 (4)	1061 (4)	809 (2)	4641 (5)	62 (5)

† *A* is O in (I) and S in (II).

Hull, 1982). The homonuclear ^{1}H chemical-shift-correlated two-dimensional diagrams were obtained by application of the COSY 45° sequence with N-type selection. Parameters were as follows: $X_1 = 256$ increments accumulated in t_1 and $X_2 = 2\text{K}$ data points in t_2; the sweep width was $SW_1 = 2016$ Hz in t_1 and $SW_2 = 4032$ Hz in t_2; $NS = 16$, recycle delay 2·25 s; zero filling in t_1 and transform with sine bell in both dimensions; spectra were symmetrized.

The sequence used in the heteronuclear shift correlation is an extension (Bax, 1983) of the standard experiment: RD-90° (^{1}H)-$t_{1/2}$-180° (^{13}C)-$t_{1/2}$-D_3-90° (^{1}H)-90° (^{13}C)-D_4-t_2 which removes J_{HH} coupling from the $F1$ domain. The spectrum was accumulated with 128 increments in t_1 and 2K data points in t_2. The spectral width was 2015 Hz in t_1 and 14 706 Hz in t_2. The delay times D_3 and D_4 were 3·33 and 1·66 ms respectively. The FID's were multiplied with a Gaussian function and zero-filled in t_1.

Data collection, structure solution and refinement

Both crystals had a prismatic shape, dimensions 0·6 × 0·4 × 0·2 mm for (I) and 0·3 × 0·15 × 0·4 mm for (II). Automatic four-circle diffractometer (Philips PW 1100), ω–2θ mode using Mo $K\bar{\alpha}$ radiation. The two data sets at 293 (2) K were recorded using similar ω–2θ scans, scan width = 1·3°, scan speed = 0·030° min^{-1}, 4081 intensities up to $\sin\theta/\lambda \le 0\cdot703$ Å^{-1}, $-15 \le h \le 15$, $k \le 13$, $l \le 12$ were collected for (I), and 4228 intensities with $\sin\theta/\lambda \le 0\cdot703$ Å^{-1} for (II), $-13 \le h \le 13$, $k \le 25$, $l \le 11$. Lattice parameters from 25 reflections ($20 < \theta < 27°$) for (I) and from 25 reflections ($20 < \theta < 27°$) for (II).

Three standard intensities monitored at intervals of 2 h showed no significant variation. Both data sets were corrected for Lorentz and polarization factors, but no absorption and extinction corrections were made.

Both structures were solved by direct methods with *MULTAN* (Germain, Main & Woolfson, 1971) using 499 reflections with normalized structure factors $E \ge 1\cdot49$ (I) and 1·52 (II). For both structures, the H atoms were obtained from a $\Delta\rho$ synthesis and adjusted to the theoretical distance from the bearing C atoms. The non-H and H atoms were refined anisotropically and isotropically, respectively, by full-matrix least squares (Sheldrick, 1976). The refinements (unit weights) converged to $R = 0\cdot058$ (I) and 0·052 (II) for all reflections with $I \ge 3\sigma$ (I), *i.e.* 1782 for (I) and 2448 for (II).

Scattering factors for S, C, N and O were taken from *International Tables for X-ray Crystallography* (1974), and for H from Stewart, Davidson & Simpson (1965). The absolute values of peaks and troughs in the final difference Fourier maps are 0·45 and 0·3 e Å^{-3} (I), and 0·24, 0·36 e Å^{-3} (II); refinements were terminated when all calculated shifts were < 0·15σ.

The atom positions corresponding to the best R values are listed in Table 1.* Table 2 gives bond lengths and angles.

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* Lists of structure factors, anisotropic thermal parameters, selected non-bonding distances and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51572 (28 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Bond lengths* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

	(I)	(II)
A^*–C1	1·480 (4)	1·841 (4)
A–C3	1·358 (4)	1·764 (4)
C1–C6	1·507 (4)	1·524 (5)
C1–C11	1·525 (5)	1·544 (5)
C1–C15	1·537 (5)	1·542 (5)
C6–C5	1·336 (4)	1·337 (5)
C6–C7	1·511 (5)	1·517 (6)
C7–C8	1·526 (6)	1·537 (6)
C8–C9	1·516 (5)	1·486 (6)
C9–C10	1·527 (6)	1·515 (6)
C5–C10	1·503 (4)	1·509 (4)
C5–N	1·416 (4)	1·409 (4)
N–C3	1·273 (4)	1·273 (4)
C3–C16	1·477 (4)	1·487 (5)
C16–C17	1·378 (4)	1·395 (5)
C17–C18	1·395 (5)	1·386 (7)
C18–C19	1·380 (6)	1·371 (6)
C19–C20	1·380 (6)	1·383 (8)
C20–C21	1·390 (6)	1·402 (7)
C21–C16	1·393 (5)	1·395 (6)
C11–C12	1·527 (6)	1·545 (5)
C12–C13	1·523 (6)	1·532 (6)
C13–C14	1·525 (7)	1·520 (6)
C14–C15	1·532 (6)	1·531 (5)
C1–A–C3	117·1 (2)	99·0 (2)
A–C1–C6	109·1 (2)	108·2 (2)
A–C1–C11	103·9 (3)	104·6 (2)
A–C1–C15	107·4 (3)	110·7 (2)
C6–C1–C11	113·6 (3)	113·3 (3)
C6–C1–C15	111·5 (3)	109·9 (3)
C11–C1–C15	110·9 (3)	109·9 (3)
A–C3–N	125·5 (3)	124·0 (3)
N–C3–C16	122·1 (3)	120·2 (3)
C3–N–C5	116·5 (3)	121·3 (3)
N–C5–C6	123·0 (3)	125·5 (3)
N–C5–C10	113·3 (3)	111·0 (3)
C6–C5–C10	123·7 (3)	123·5 (3)
C1–C6–C5	118·4 (3)	121·4 (3)
C1–C6–C7	118·6 (3)	116·8 (3)
C5–C6–C7	122·9 (3)	121·5 (3)
C6–C7–C8	112·2 (3)	112·7 (3)
C7–C8–C9	111·4 (3)	111·2 (3)
C8–C9–C10	111·1 (3)	111·2 (3)
C5–C10–C9	111·7 (3)	112·9 (3)
C1–C11–C12	112·5 (3)	112·7 (3)
C11–C12–C13	110·9 (4)	110·7 (3)
C12–C13–C14	110·8 (4)	111·0 (3)
C13–C14–C15	111·6 (4)	111·6 (3)
C1–C15–C14	112·6 (3)	113·2 (3)
C3–C16–C17	121·8 (3)	122·4 (3)
C17–C16–C21	118·9 (3)	118·5 (3)
C16–C17–C18	120·3 (3)	120·0 (4)
C17–C18–C19	119·4 (3)	121·1 (4)
C18–C19–C20	120·0 (4)	119·7 (5)
C19–C20–C21	120·0 (4)	120·2 (5)
C16–C21–C20	120·2 (3)	119·9 (4)

* *A* is O in (I) and S in (II).

Table 3. ^{1}H *and* ^{13}C *chemical shifts of compound* (I) *and its thia* (II) *and selena* (III) *homologs*

	(I)		(II)		(III)	
C/H atoms	δ_C (p.p.m.)	δ_H (p.p.m.)	δ_C (p.p.m.)	δ_H (p.p.m.)	δ_C (p.p.m.)	δ_H (p.p.m.)
1	78·61		48·79		50·76	
3	154·30		155·30		156·15	
5	134·25		139·38		140·74	
6	120·26		121·19		121·66	
7	23·59	1·77	24·56	1·98	24·87	2·03
8	23·11	1·44	23·60	≅1·55	23·79	~1·55
9	23·09	1·54	23·05	≅1·55	23·03	~1·55
10	30·10	2·44	31·94	2·62	32·34	2·64
11,15	32·66	1,27,1·87	33·68	1·41, 1·70	34·58	1·47,~1·75
12,14	21·25	1·85,1·37	21·91	1·80, 1·32	23·20	~1·75,1·34
13	25·63	0·99,1·60	26·20	0·94,≅1·55	26·35	0·94,~1·55
16	135·98		141·78		143·86	
17,21	127·95	7·82	128·39	8·25	128·53	8·25
18,20	128·29	6·62	128·51	7·10	128·90	7·15
19	130·71	6·62	130·77	7·10	130·78	7·15

similarity of structure. Integrations of proton spectra and carbon multiplicities determination using the *DEPT* sequence (Doddrell, Pegg & Bendall, 1982) are compatible with the formula $C_{19}H_{23}NX$. Spectral editing reveals nine methylene, five methine and five quaternary C atoms. Carbon spectra show that there are two equivalent C atoms at $\delta = 32·66$ and 21·25 p.p.m. for (I), at $\delta = 21·91$ and 33·68 p.p.m. for (II) and at $\delta = 23·20$ and 34·58 p.p.m. for (III).

The presence of an amide C atom can be ruled out since the chemical shift of an amide C should be approximately 170 p.p.m. for the oxa compound and 200 and 205 p.p.m. for the thia and selena homologs, respectively (Andersen, Guziec, Wong, Murphy & Cullen, 1982). Moreover, in contrast to the oxygen or sulfur analogs, one of the six naturally occuring selenium isotopes (^{77}Se, natural abundance 7·6%) possesses a magnetic spin moment of $I = \frac{1}{2}$ which should be adequately reflected in the ^{13}C NMR satellite subspectrum of the selena compound. For a selenoamide, the magnitude of $^1J(^{77}$Se–^{13}C) is 210–220 Hz (Andersen *et al.*, 1982). This is not what is observed in the carbon spectrum of the selena homolog. All these considerations permit the spiro structures (IX) to be excluded unambiguously.

Results and discussion

NMR

Compounds (I) and (II) and the selenium homolog (III) were analyzed in solution by NMR spectroscopy. For the oxa derivative (I), two-dimensional NMR experiments were needed to interpret the spectra. Further details of two-dimensional NMR may be found in review articles (Freeman, 1980; Been & Gunther, 1983; Morris, 1986; Bax, 1982). In the following discussion, the molecular numbering defined in the X-ray structure analysis will be used.
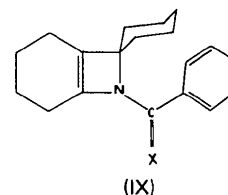
A mere examination of the ^{1}H and ^{13}C (Table 3) NMR spectra of the three compounds clearly reveals a

(IX)

The chemical shift of the C3 atom is compatible with an imidate structure (Meese & Walter, 1985). The shift of 154·3 p.p.m. for C3 in compound (I) is in accord with data in the literature for related 1,3-oxazines (Altman, Gilboa & Ben-Ishai, 1977). Taking into account the chemistry involved, the compounds clearly have the structures (I)–(III).

Assignments of the other C atoms were obtained for the oxa compound and transposed for the thia and selena homologs. The assignment of quaternary C atoms is rather straightforward owing to their proximity to heteroatoms. Assignment of C16 at $\delta = 135.98$ p.p.m. was obtained by comparison with the hydrogenation products, *cis*- and *trans*-cyclohexanespiro-2-(4-phenyl-5-aza-3-oxabicyclo[4.4.0]dec-4-ene) (Bochu, Couture & Lablache-Combier, 1989). A two-dimensional experiment correlating carbon and proton shifts was needed for the interpretation of the protonated C atom (Fig. 1). The methylene groups with non-equivalent protons give rise to two distinct signals which permitted the conclusion that the cyclohexane ring is in the favored chair conformation in agreement with the molecular structure in the solid state.

The assignment of the aliphatic part of the proton spectrum was completed through a COSY-45 two-dimensional experiment. Protons belonging to the cyclohexene and to the cyclohexane rings were unambiguously located (Fig. 2).

The proton at 0.99 p.p.m. is in the axial position and appears as a quadruplet ($J = 13.1$ Hz) of triplets ($J = 3.7$ Hz). This pattern results from the identical value of the germinal coupling and of the vicinal axial–axial coupling; the smallest coupling is between axial and equatorial H atoms (Martin & Martin, 1971). Homodecoupling experiments enable the shifts of the proton in the axial (see first value in Table 3) and equatorial positions to be determined. The measurement of all the proton coupling constants was not possible due to overlaps of multiplets, strong coupling and the occurrence of many small coupling constants.

For the selena compounds (III) no crystals were available; nevertheless, its carbon spectrum shows that
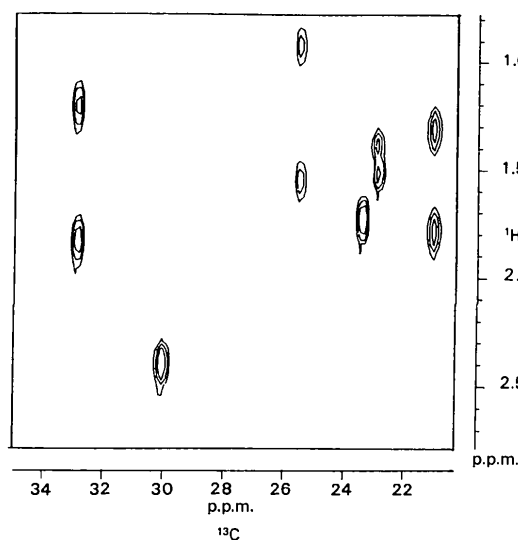
the conformation of the molecule is similar to that of the two former derivatives. Atoms C1 and C3 are flanked with [77]Se satellites corresponding to coupling constants of 52.3 and 135.2 Hz respectively. It has been noted that a magnitude of 45 Hz or more for $J(^{77}Se-^{13}C)$ is indicative of a direct C–Se bond. NMR coupling constants between [77]Se and ^{13}C are known to be affected by the hybridization of the C atom α to the Se atom. Typically, the magnitude of $^1J(^{77}Se-^{13}C)$ reported in the literature is approximately 50–75 Hz for a C–Se single bond with an sp^3 carbon and 110–140 Hz with an sp^2 carbon depending on the degree of partial C–Se double-bond character (Cullen, Guziec, Murphy, Wong & Andersen, 1981; Meese & Walter, 1985). These results show that the Se atom is linked to the spiro C atom of the cyclohexane ring and to the imido C atom. Attempts to measure $^2J(^{77}Se-^{13}C)$ and

Fig. 1. 400 MHz $^1H-^{13}C$ shift-correlated two-dimensional NMR spectrum of (I) (aliphatic region).
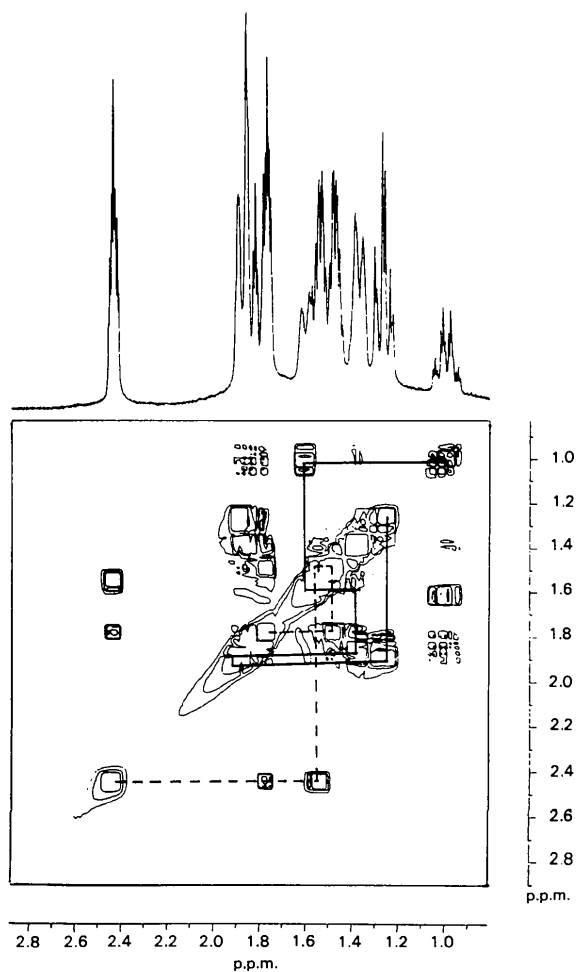

Fig. 2. 400 MHz ^1H shift-correlated two-dimensional NMR spectrum of (I) (aliphatic region). Correlations for the cyclohexane and cyclohexene rings are indicated by dashed and full lines, respectively. The upper trace corresponds to the one-dimensional spectrum.

$^3J(^{77}Se-^{13}C)$ coupling constants were not conclusive, their magnitude being less than 10 Hz.

X-ray diffraction

Molecular geometry. The cyclohexane rings have the same chair conformation in both structures [the distances between C1 and C13 and the mean plane are 0·635 (3), −0·673 (4) Å for (I), and 0·645 (3), −0·669 (4) Å for (II)]. The replacement of the O by the S atom brings some changes in the 2-spiro-3-oxa group; the bond angles adjacent to the heteroatom decrease while larger values are observed for the C6—C5—N angle. We note also an important contraction of the C8—C9 bond when an S atom replaces the O atom. The mean plane through the atoms of the bicyclo group (Table 5) shows a larger distortion in compound (II),

C1 and C9 are, for instance, farther from the mean plane in the compound with S atom. The torsion angles reported in Table 4, the angles between sheeted planes (Table 5) and a Newmann projection along the C3—C16 bond (see below) complete the description of each molecule and emphasize the discrepancies between them.
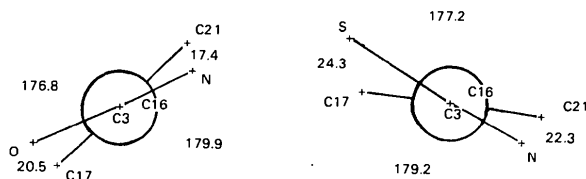
No quantitative comparisons can be made concerning the conformation of the molecule in the liquid and solid states except that in both states the chair conformation is favored for the cyclohexane ring. A thermal analysis of the molecules in the crystal using the procedure proposed by Schomaker & Trueblood (1968) shows in both structures an isotropic translation of the whole molecule (Table 6), while the rotational motion in the two cases is quite negligible and the fit of calculated U_{ij} terms to those observed is better for the molecule containing the O atom. Without the benzene ring, the agreement between the calculated and observed U_{ij} is better in the sulfur compound, showing that this part of the molecule is reasonably rigid (the e.s.d. on this difference is 0·0023 Å² compared with an estimated precision of the U_{ij} from least-squares refinements of 0·0025 Å²). This rigidity is certainly related to the nature and strength of the interactions between the H atoms of the cyclohexane ring and the electronic cloud of the S atom; however, there is no intramolecular hydrogen bond.

In a second calculation, all the atomic vibrations were fitted by the rigid-body plus non-rigid librating group (TLS + Ω) model of Dunitz & White (1973) and Trueblood (1978). The non-rigidly attached benzene ring undergoes torsional oscillations around the C3—C16 bond with r.m.s. amplitudes of 4·09 (1·1) and 5·02 (1·5) for (I) and (II), respectively.

These values confirm our previous remarks and are in agreement with the observed shape of the thermal ellipsoids (Fig. 3).

Table 4. Torsion angles (°) of some interesting parts of the molecules

	(I)	(II)
C11—C1—*A*—C3	−157·7 (4)	−166·3 (3)
C11—C1—C6—C5	−141·9 (4)	−153·3 (4)
C11—C1—C6—C7	41·7 (3)	32·9 (3)
C15—C1—*A*—C3	84·7 (4)	75·3 (3)
C15—C1—C6—C7	−84·4 (3)	−90·4 (4)
C15—C1—C6—C5	91·9 (3)	83·3 (4)
A—C3—C16—C17	−20·5 (3)	−24·3 (3)
A—C3—C16—C21	159·4 (4)	154·9 (4)

* *A* is O in (I) and S in (II).

Table 5. *Mean planes*

Deviations from plane (Å) with e.s.d.'s in parentheses

	(I)	(II)
A*	0·199 (2)	0·162 (1)
N	−0·236 (3)	−0·306 (2)
C1	−0·264 (3)	−0·619 (4)
C3	−0·046 (3)	−0·187 (4)
C5	−0·116 (3)	−0·091 (4)
C6	−0·093 (3)	−0·205 (4)
C7	0·013 (4)	−0·073 (4)
C8	−0·218 (4)	−0·128 (4)
C9	0·503 (4)	0·715 (4)
C10	0·005 (4)	0·239 (4)

Angles (°) between planes†

	(I)	(II)
P_1–P_2	8·8	14·1
P_1–P_3	70·6	61·9
P_2–P_3	77·1	61·9

* *A* is O in (I) and S in (II).
† Atoms in the least-squares planes are as follows: $P_1 = A$, N, C1, C3, C5, C6, C7, C8, C9, C10; P_2 = C16, C17, C18, C19, C20, C21; P_3 = C11, C12, C14, C15.

Table 6. *Rigid-body vibration parameters for all the heavy atoms of* (I) *and* (II)

	(I)			(II)		
T (Å²) × 10⁻⁴	388 (11)	16 (11)	−7 (9)	335 (14)	14 (13)	−16 (14)
		323 (14)	16 (11)		301 (15)	16 (14)
			338 (11)			353 (17)
L (rad²) × 10⁻⁴	29 (2)	8 (1)	11 (1)	26 (2)	0 (2)	7 (2)
		12 (2)	8 (11)		18 (2)	8 (2)
			24 (2)			19 (2)
S (Å × rad) × 10⁻⁶	244 (528)	−1595 (265)	−366 (312)	−434 (602)	−79 (435)	332 (340)
	330 (272)	−256 (422)	854 (218)	1735 (355)	307 (545)	−130 (300)
	−826 (380)	−757 (262)	−8 (3956)	1974 (344)	−1155 (345)	127 (5141)
R.m.s. (U^o-U^c) (Å²)	0·0036	0·0030	(Excluding the	0·0047	0·0023	(Excluding the
E.s.d. U_{ij}^{obs} (Å²)	0·0040	0·0034	benzene ring)	0·0051	0·0026	benzene ring)

Molecular packing. Fig. 4 illustrates the packing of the molecules in the plane (101) for the oxa compound and (110) for the thia derivative. No intermolecular distances are less than the sum of the van der Waals radii of the atoms involved, except the S–S distance (3·67 Å) which is just at the limit of the sum of the van der Waals radii.

For the oxa compound, the mean plane of the molecule (excluding the cyclohexane ring) is almost in the plane (101). The packing of the molecules can be described in terms of columns almost parallel to the **b** direction.

Concluding remarks

The one- and two-dimensional NMR studies allow an almost complete assignment of the ^1H and ^{13}C resonances of the different compounds. The conformations of the molecules in solution are almost identical and should also be very similar to those obtained in the solid state.
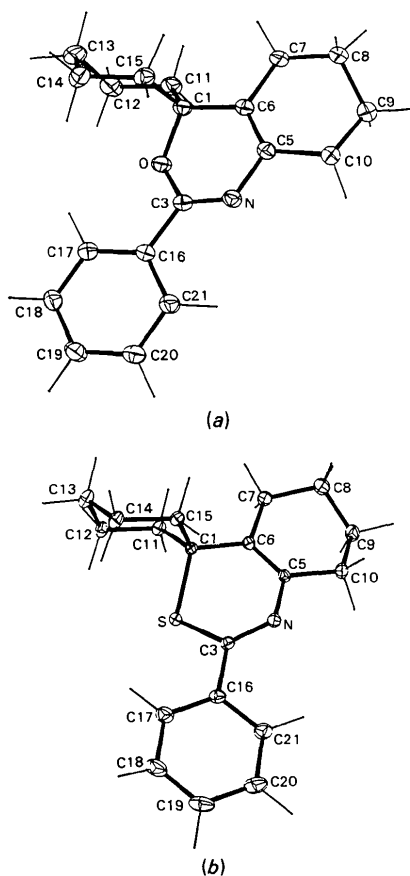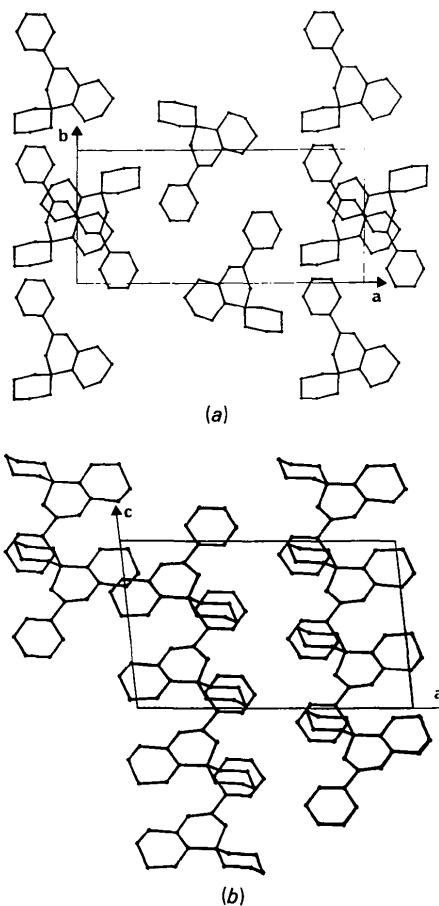

(a)

(b)

Fig. 4. Packing (a) projection along **b** of (I) and (b) projection along **c** of (II) (ORTEP; Johnson, 1976).

(a)

(b)

Fig. 3. Perspective view of the molecules (a) (I) and (b) (II) (ORTEP; Johnson, 1976).

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Three-Dimensional Electron Diffraction Structure Analysis of Polyethylene

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Abstract

The electron diffraction patterns of four zones, (0kl), (1kl), (hhl) and (k+l,k,l), were obtained from polyethylene epitaxially crystallized on benzoic acid. During evaluation of the data it was shown that incoherent multiple scattering is the main cause of perturbations of reflection intensity, a fact consistent with electron microscopic observations of multilayer crystal morphology. After correction for incoherent scattering, a three-dimensional structural analysis confirmed that the epitaxial crystals have orthorhombic chain packing in the $O_\perp$ subcell, *i.e.* the space group *Pnam*. The analysis, which involved combining the data of epitaxially grown crystals with those of crystals grown from solution, gave an R factor of 0·207 for a setting angle of 46·7°. At a significance level of 0·05, the accepted range of the chain setting angles is 44·5–49·6°.

Introduction

Given the availability of microcrystalline samples, three-dimensional electron diffraction structure analysis would be an ideal way to obtain more accurate conformational characteristics of polymer chains. So far only a small number of polymer structures has been based on three-dimensional structural analysis with electron diffraction data. The problem is how to correct various zonal data and how to obtain a nearly complete set of normalized three-dimensional intensities, requirements for which, up to now, there is very little experience. Various zonal patterns come from different microcrystals, which may experience different perturbative effects, including beam-induced radiation damage, bend deformation, *n*-beam dynamical diffraction and incoherent multiple scattering. Which of these is the major factor often depends on the morphology of microcrystal growth.

The orthorhombic packing of polyethylene (PE) with space group *Pnam* was determined by Bunn (1939) by an X-ray diffraction study of PE fibres which was based on 25 unique intensity data, three of which were from overlapped reflections. Recent determinations of the PE crystal structure by electron diffraction of the (hk0) zone from solution-grown crystals have shown that the molecular packing in the microcrystalline state is also *Pnam* and the setting angle φ, *i.e.* the angle the chain zigzag makes with the *b* axis (see Fig. 1*a*), is about 42° (Dorset & Moss, 1983). Nevertheless, solution-crystallized samples provide incomplete information (Dorset, 1985), principally as a result of limited data resolution, but also because the data are restricted to a single zone. On epitaxial orientation, PE crystallizes on the (001) crystal faces of benzoic acid (BA) (Wittmann, Hodge & Lotz, 1983) to project a view onto the molecular chains. Nevertheless, in earlier studies of PE, electron diffraction patterns were ambiguous (Wittmann, Hodge & Lotz, 1983; Moss, Dorset, Wittmann & Lotz, 1985–1986) since the zonal patterns were contaminated with contributions from upper layers, *i.e.* some reflections from different zones overlapped, leading to incorrect measurement of the