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A ^{13}C and ^{1}H NMR Study of 1-Pyrazolino [4.3-*c*]cephalosporins and Their Oxidized Derivatives

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The presumed conformation of the title compounds (*1a–d*) is in accordance with the ^{1}H NMR data of other known cepham derivatives. Information gained from the ^{13}C NMR investigations shows that the effects of oxidation can reasonably be explained in conformity with examples of other types to be found in the literature.

The cycloaddition of diazomethane to the 4-nitrobenzyl ester of 7-phenoxyacetamido-3-methyl-3-cephem-4-carboxylate (*3a*) was earlier found to lead to the regio- and stereospecific formation of one product,[1] to which structure *1a* was assigned. We now report a ^{13}C and ^{1}H NMR study of *1a–d* in order to confirm the previous conclusions.

Only scattered information is available on the ^{13}C NMR spectroscopy of cephams.[2–4] More data can be found on various sulfoxides and sulfides, although systematic investigations have been carried out only on simple systems (for reviews, see Refs. 5b and 6).

EXPERIMENTAL

^{1}H NMR spectra of *1a–d* and *3a–d* were run on a JEOL MH 100 spectrometer, in DMSO-d_6 with TMS as internal standard. ^{13}C NMR spectra were measured at natural abudance on a JEOL FX 60 spectrometer in DMSO-d_6 and in pyridin-d_5 relative to TMS. Data were collected over a 4 KHz sweep width in 4 K of memory using a tip angle of 45° and 2–4 sec repetition times. Coupled spectra were obtained in gated I mode. ^{1}H noise off-resonance and SFORD decoupled spectra were measured for each compound.

DISCUSSION

Molecular models show that the tetrahydrothiazine ring in *1a–d* can adopt two conformations: A and B (Fig. 1). The triple condensed ring system means that only the S–C-2–C-3 moiety of the tetrahydro thiazine can assume a structure similar to that in cyclohexane. In the case of conformation A the $S(\beta)$ axial oxygen of the sulfoxide group is *syn-anti* to H-2_α, but the dihedral angle between the *syn*-clinal Me-3_α and H-2_α is already smaller than it would be in a "pure" *gauche* position. The steric relations between the oxygens and C-2 hydrogens are reversed in conformation B. $^{1}H-\{^{1}H\}$–NOE investigations indicate that the conformation of substituted cephams *2a–d*, a related case found in the literature,[3] is analogous to A.

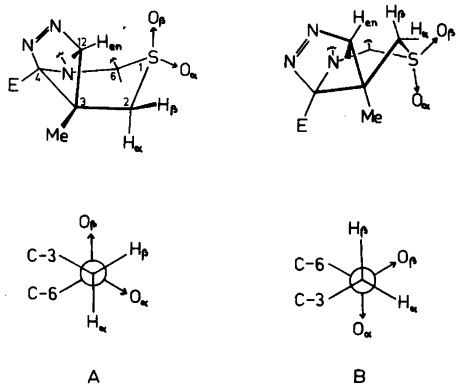

Fig. 1. The two possible conformations of *1a–d*. For clarity the β-lactam ring is omitted.

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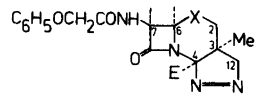
Table 1. ^{1}H NMR data of the cycloadducts *1a–d*.



1a-d E = -$COOCH_2C_6H_4$-pNO_2

X	H-2α(ax)	$\Delta\delta H_{2ae}$	H-2β(eq)	H-6	H-7	H-12en	$\Delta\delta H_{12ee}$	H-12exo	Me-3
1a S	3.04[a]		3.04	5.28	5.52	4.78	0.22	5.00	1.07
1b R(α)eq S→0	3.02 (0.02)[b]		3.02 (0.02)	4.75 (0.53)	5.61 (−0.09)	4.53 (0.25)	0.39	4.92 (0.08)	1.17 (−0.1)
1c S(β)ax S→0	2.98 (0.06)	0.94	3.92 (−0.88)	5.27 (0.01)	5.98 (−0.46)	5.54 (−0.76)	0.68	4.86 (0.16)	0.81 (0.26)
1d SO_2	3.57 (−0.56)	0.32	3.89 (−0.81)	5.38 (−0.1)	6.01 (−0.5)	5.09 (−0.31)	0.12	4.97 (0.03)	0.92 (0.15)

[a] ppm values in δ units relative to TMS in DMSO-d_6. [b] Chemical shift differences in parentheses from the same proton of the sulfide. A positive value denotes an upfield shift and *vice versa*.

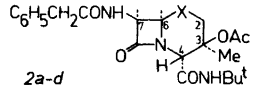
DISCUSSION OF ^{1}H NMR RESULTS

Chiral sulfoxides produce an orientation-dependent shielding or deshielding in their immediate environment. This diamagnetic anisotropy is said to possess an acetylene-type anisotropy although this concept has been criticized in view of the anomalies found so far.

In ^{1}H NMR spectra the C-2 protons of cephems usually appear as AB quartets, although this does not hold for *1a*. In contrast to the sulfoxides, the equatorial proton of cephalosporin-sulfides is assigned at higher field. On the other hand, if the sulfoxide group has an axial lone-pair of electrons, the shift difference $\Delta\delta H_{2ae}$* between the axial and

* The following abbrevations are used for chemical shift differences *e.g.*:
$\Delta\delta H_{2ae} = \delta H_{2ax} - \delta H_{2eq}$
$\Delta\delta H_{2ax} = (\delta H_{2ax})_{\text{axial SO}} - (\delta H_{2ax})_{\text{equatorial SO}}$

Table 2. ^{1}H NMR data of the cephams *2a–d*.

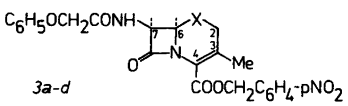


2a-d

X	H-2α(ax)	$\Delta\delta H_{2ae}$	H-2β(eq)	H-6	H-7	H-4	Me-3
2a S	3.75[a]		3.20	5.30	5.58	4.40	1.54
2b R(α)eq S→0	3.30 (0.45)[b]	0.5	3.80 (−0.6)	4.24 (1.46)	5.27 (0.31)	4.90 (−0.5)	1.65 (−0.11)
2c S(β)ax S→0	3.35 (0.4)	0.98	4.33 (−1.13)	4.97 (0.33)	6.00 (−0.42)	4.6 (−0.2)	1.58 (−0.04)
2d SO_2	4.07 (−0.32)	0.17	3.90 (−0.7)	5.14 (0.16)	6.00 (−0.42)	4.44 (−0.04)	1.57 (−0.03)

[a,b] See footnotes to Table 1. Data from Ref. 29.

Table 3. ^{1}H NMR data of the cephems *3a–d*.



3a-d

X	$H_{2\alpha}$(ax)	$\Delta\delta H_{2ae}$	$H_{2\beta}$(eq)
3a *S*	3.55[a]	0.3	3.25
3b *R*(α)eq S→0	3.69	0.54	4.23
	(−0.14)[b]		(−0.98)
3c *S*(β)ax S→0	3.67	0.31	3.98
	(−0.12)		(−0.73)
3d SO_2	4.06	0.34	3.72
	(−0.51)		(−0.47)

[a,b] See footnotes to Table 1.

equatorial protons is usually greater then in the opposite case.[6–8] It is true for cephem-sulfoxides (Table 3), but not for *2b* and *c* (Table 2) and the cycloadducts *1b* and *c* (Table 1). The axial→equatorial sulfoxide reversal usually causes a smaller effect at axial hydrogens ($\Delta\delta = \sim 0.2$ ppm);[6,8,9] a similar relation can be deduced from the chemical shift data on *3b–c*, *2b–c* and *1b–c* ($\Delta\delta H_{2ax}$ = 0.02, 0.05 and 0.04 ppm; $\Delta\delta H_{2eq}$ = 0.25, 0.53 and 0.9 ppm, respectively). The H-2_{eq} proton in the *R*(α)-equatorial cephem-sulfoxide *3b* is deshielded relative to the *S*(β)-axial sulfoxide, while in the case of cephams *2b–c* and cycloadduct sulfoxides *1b–c* shielding is seen. The reason for this is uncertain, because the difference in dihedral angle between the *S*(β)-sulfoxide oxygen and H-2_{eq} in derivatives of *1 vs. 2* and *3* is not great enough to confirm this phenomenon. As a whole, the above-mentioned ^{1}H resonance data on *1a–c* and *2a–c* show that the changes in resonance have parallel trends pointing to related (*i.e.* A) conformations.

$\Delta\delta_{2ae}$ for the cycloadduct sulfone *1d* is greatly reduced, similarly as for other sulfones.[7,10] Two possible interpretations could account for this: (a) The sulfone group possesses a diamagnetic anisotropy considerably different from that of the sulfoxide group (similar to that proposed for the nitro group);[11] (b) the lack of a lone-pair in the sulfone could theoretically bring about a similar effect (*cf.* an assumed $n \rightarrow \sigma^*$ interaction between the axial lone-pair and the *anti*-periplanar hydrogens in *N*-heterocycles[12]), the loss of this influence results in a lessening of $\Delta\delta H_{2ae}$, but these assumptions would lead to contradictions in sulfoxides of *1* and *2*.

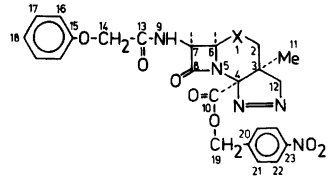
The condensed pyrazoline ring in compounds *1a–d* is less puckered than in a monocyclic 1-pyrazoline ring. It is known[13,14] that the pseudo-axial protons of 1-pyrazolines with an envelope conformation resonate at higher fields. The signal at 4.78 ppm in *1a* was tentatively assigned to the 12-*endo* hydrogen, in accordance with the fact that the dihedral angle between the *endo* C–H bond and the C-3–C-4 bond is about 20° smaller than the corresponding *exo* angle. If it is assumed that the chemical shift of the *exo* hydrogen is less influenced by changes in the oxydation state of the sulfur, and the chemical shift parameters are assigned as shown in Table 1, it is understandable that in the case of the *R*(α)-sulfoxide *1b* the *endo* proton is situated in the shielding cone of the sulfoxide bond ($\Delta\delta H_{en}$ = 0.25 ppm), while in the *S*(β)-sulfoxide *1c* it is strongly deshielded ($\Delta\delta H_{en} = -0.76$ ppm). A similar but smaller deshielding is also seen in *1d*. For a related example see Ref. 30. The spatial proximity of a lone-pair – if the geometry is fortunate – can also cause deshielding in certain cases,[16,17] but here, if any, it should then appear in *1a* and *b*.

The ^{1}H NMR signals of H-6 in *1a–d* are similar to those usually found in other β-lactam compounds, *i.e.* a higher shielding in the *R*(α)-sulfoxide and deshielding in the sulfone.[18]

^{13}C NMR RESULTS

The oxidation state of the sulfur also has a characteristic influence on the ^{13}C NMR resonance of C-2, C-3 and C-6 (see Table 4; Table 5 contains a concise summary of the more important shift parameters and differences). It is regarded of general validity that in 6-membered carbo- and heterocycles an axial substituent causes smaller downfield shifts at C-2 and C-6 (β-effect) and larger upfield shifts at C-3 and C-5 (γ-effect) than in the case of an equatorial substituent.[21] This is apparent from the data on C-2 and C-3 of the cycloadduct (Table 5), in line with those for other thiane derivatives, and can also be observed in penicillins and cephalosporins.[2] This phenomenon of shielding differences caused by the two sulfoxide isomers at C-2 was found by Buchanan and Durst[22] *via* electric field calculation to be about 9 ppm. In the cases of *1b* and *c* this difference 8 ppm agrees well. In the sulfone *1d* there is an additional −1.6 ppm down-

Table 4. ^{13}C-NMR data of the cycloadducts *1a–d*.



1a X = S
1b X = S→O R(α)
1c X = S→O S(β)
1d X = SO_2

Carbon	*1a*	*1b*	*1c*	*1d*
2	31.2 (145 t) [b]	51.7 (142 t)	43.7 (135 t)	53.3 t
	30.0 (143 t)	50.0	–	51.8 t
3	39.7 s	58.5 s	37.6 s	47.8 s
	–	57.1	–	46.6
4	99.9 s	82.0 s	96.9 s	98.0 s
	98.7	80.6	96.0	96.5
6	57.7 (174 d)	73.9 (174 d)	67.3 (170 d)	67.4
	55.8 (172 d)	72.2 (178 d)	66.2 (172 d)	67.1 (172 d)
7	60.4 (152 d)	60.7 (152 d)	58.9 (152 d)	60.2
	59.1 (154 d)	59.1 (152 d)	57.4 (152 d)	58.4 (156 d)
8[a]	166.0 s	166.3 s	166.2 s	165.7 s
	164.8	165.1	164.8	164.0
10[a]	163.0 s	165.0 s	163.6 s	162.8 s
	161.7	163.6	162.2	161.8
11	20.9 (123 q)	18.8 (131 q)	24.2 (131 q)	22.2
	20.0 (127 q)	17.9 (131 q)	23.6 (133 q)	21.6 (130 q)
12	85.4 (143 t)	–	86.4 (141 t)	85.5
	85.1 (148 t)	–	86.4 (148 t)	85.2 (145 t)
13[a]	169.6 s	170.0 s	168.5 s	169.2 s
	168.2	168.4	167.9	168.2
14	67.9 (147 t)	67.8 (145 t)	67.3 (148 t)	68.5
	66.2 (147 t)	66.2 (146 t)	66.2 (150 t)	66.1 (147 t)
15	159.2 s	158.3 s	157.8 s	158.0 s
	157.4	157.2	157.0	157.3
16	115.1 d	115.0 d	115.1 d	115.1 d
	114.4 (160 d)	114.4 (162 d)	114.5 (162 d)	114.4 (160 d)
17	129.2 d	129.8 d	129.8 d	129.9 d
	129.2	129.2 (168 d)	129.5 (162 d)	129.5 (160 d)
18	–			
	121.0 (162 d)	121.0 (162 d)	121.4 (160 d)	121.2 (154 d)
19	66.6 (150 t)	66.8 (148 t)	67.3 (148 t)	67.4
	66.2 (147 t)	66.2 (146 t)	66.2 (150 t)	67.1 (150 t)
20	142.5 s	–	–	142.0 s
	142.2 s	142.5 s	142.2 s	142.2 s
21	129.7 d	129.3 d	129.4 d	129.4 d
	129.2 (164 d)	129.2 (168 d)	129.5 (162 d)	129.5 (160 d)
22	–			
	123.5 (172 d)	123.5 (170 d)	123.5 (170 d)	123.6 (170 d)
23	–			
	147.1 s	147.1 s	147.3 s	147.3 s

[a] For assignment of carbonyl carbons, see Refs. 19 and 20. [b] ppm values obtained in pyridine-d_5 (upper values) and in DMSO-d_6 (lower values).

Table 5. Selected ^{13}C NMR data of *1a–d*.

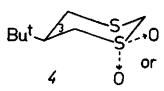
X		C-2	C-3	C-4	C-11	C-12	C-6	C-7
1a	*S*	31.2[a]	39.7	99.9	20.9	85.4	57.7	60.4
1b	*R*(α)eq S→O	51.7 (−20.7)[b]	58.5 (−18.8)	82.0 (17.9)	18.8 (2.1)	– –	73.9 (−16.2)	60.7 (−0.3)
1c	*S*(β)ax S→O	43.7 (−12.5)	37.6 (2.1)	96.9 (3.0)	24.2 (−3.6)	86.4 (−1.0)	67.3 (−9.6)	58.9 (1.5)
1d	SO_2	53.3 (−22.1)	47.8 (−8.1)	98.0 (1.9)	22.2 (−1.3)	85.5 (−0.1)	67.4 (−9.7)	60.2 (0.2)

[a] ppm values in δ units downfield from TMS (in pyridine-d_5). [b] Data in parentheses are shift differences relative to the sulfide; a positive value means an upfield shift.

field shift relative to the *R*(α)-sulfoxide. The deshielding of C-2 in sulfones (compared to the corresponding equatorial sulfoxide) varies appreciably: the effect is very small in aliphatic sulfones,[21] −0.5 ppm in the unsubstituted thiane[7,22] and −4.6 ppm in oxathiane.

The behavior of C-6 of the β-lactam ring parallels that of C-2, *i.e.* there is a greater deshielding in the *R*(α)-sulfoxide *1b*. This downfield shift of C-2 and C-6 is similar to that found in 3-chlorocephams.[3a,4]

The C-3 carbon is shielded by 2.1 ppm in the axial sulfoxide *1c* and by 20.9 ppm relative to the equatorial sulfoxide. This shielding, often referred to as the steric *γ-gauche* effect,[23] is also characteristic of other thiane-sulfoxides and sulfilimines,



e.g. it is 7.8 ppm in thianes (Table 8) and 16.3 ppm in the anchored dithiane derivative *4*.[5b] This proves the assumed conformation A, as in the other case this *γ-gauche* effect should appear in the *R*(α)-sulfoxide. However, problems arise in the sulfones,[10,11,24] for in spite of the further presence of the *γ-gauche* interaction this shielding is strongly reduced.

Sulfoxide and sulfone γ-effects. For a detailed insight into this problem, the four possible γ-effects must be taken into consideration (see Fig. 2). If it is assumed that the through-bond electronic effect of a lone-pair is smaller in the *gauche* position, *i.e.* $\gamma_{gauche}^{lone-pair} < \gamma_{anti}^{lone-pair}$, the shift difference $\Delta\delta SO_{eq} -$

SO_{ax}: $\gamma_{gauche}^{O} + \gamma_{anti}^{lone-pair}$
SO_{eq}: $\gamma_{anti}^{O} + \gamma_{gauche}^{lone-pair}$
SO_2: $\gamma_{gauche}^{O} + \gamma_{anti}^{O}$

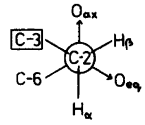


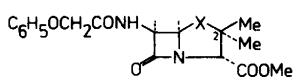
Fig. 2. γ-effects between C-3 and the sulfoxide group in configuration A.

SO_2 on C-3 will to a first approximation reflect the γ_{gauche}^{O} effect of the oxygen, while, in turn, the difference $\Delta\delta SO_{ax} - SO_2$ is characteristic of the $\gamma_{anti}^{lone-pair}$ effect. In other words, it is better to say that a ring carbon *anti*-periplanar to the lone pair of the sulfur is shifted upfield. This effect is about 6–10 ppm in thiane derivatives,[10,21,22] 8–9 ppm in sulfilimines[25] and 10 ppm in nitrogen heterocycles.[5] Thus, a clearer view of the influence of the sulfoxide lone-pair on C-3 can be obtained, if differences Δδ are formed from the shift data of the sulfone and sulfoxide derivatives, rather than using the parent sulfide as reference. In this way the influence of inductive effects of electrostatic types is decreased, as they exhibit a smaller change in the

Table 6. Shift differences for C-3 of *1b–d*.

X		C-3 ppm	$\Delta\delta_{SO-SO_2}$
1b	$R(\alpha)_{eq}$ S→O	58.5	−10.7
1c	$S(\beta)_{ax}$ S→O	37.6	10.2
1d	SO_2	47.8	

Table 7. Shift differences for Me-2 of 1-oxides of penicillin V methyl ester.



X	Me-2β ppm[a]	Me-2β $\Delta\delta_{SO-SO_2}$	Me-2α ppm	Me-2α $\Delta\delta_{SO-SO_2}$
$R(\alpha)_{eq}$ S→O	24.3	−4.3	16.0	1.7
$S(\beta)_{ax}$ S→O	19.3	0.7	18.4	−0.7
SO_2	20.0		17.7	

[a] ppm in δ units, taken from Ref. 2b.

SO_2→SO reversal than they do in the S→SO case.[26] The shift differences $\Delta\delta SO-SO_2$ for *1b–d* are shown in Table 6, and reveal that the equatorial lone-pair shields the C-3 resonance. To assess the generality of this phenomenon, let us consider the 2β- and 2α-methyl groups of penicillin derivatives (Table 7) as well as the thiane oxides (Table 8). A related *γ-anti* effect caused by second-row heteroatoms on carbon atoms is discussed in Ref. 31.

The effect can clearly be seen even in the case of penicillin sulfoxides, despite the fact that in the thiazolidine ring the dihedral angle between the *trans* methyl group and the lone-pair is smaller than that in the *anti*-periplanar arrangement in cephams.

The pyrazoline C-12 signal in the ^{13}C NMR spectrum of *1b* is not understandable. In the case of this compound a δ-effect of 3–4 ppm would be expected; in fact this signal cannot be found using different solvents and decouplings. At first sight, plausible possibilities were (1) the presence of an *N*-oxide in the pyrazoline ring, (2) a 2-pyrazoline was formed or, as a consequence of (1) or (2), (3) accidental signal coincidence. Against the first two assumptions is the fact that *1b* has a mass-spectrum characteristic of 1-pyrazolines (loss of N_2)[1] and a satisfactory ^1H NMR spectrum; in addition, formation of an *N*-oxide would have caused another type of shift.[28] On the other hand, signal coincidences could be resolved using another solvent. Probably relaxation effects are responsible for this phenomenon.

Table 8. Shift differences for C-3 of thiane 1-oxides.

X	C-3 ppm[a]	C-3 $\Delta\delta_{SO-SO_2}$
S	(27.9)[27]	(−2.8)
S→O ax	15.5[22]	9.6
S→O eq	23.3[22]	1.8
SO_2	25.1[7]	

[a] The given lit. data were obtained in $CDCl_3$ or CD_2Cl_2 solutions.

Note added in proof. A more recent X-ray study on compound *1a*, confirming the proposed structure in this article. will appear in *J. Mol. Struct.*

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