IR Spectroscopy. The IR spectra of the α-diazo ketones, of the reaction mixtures, and of certain authentic reaction products were recorded in the gas phase and in solution (CCl_4) with a FT IR spectrometer (Nicolet 7199) equiped with an MCT detector in the range 4000–400 cm^{-1}. For certain IR absorption bands of 1 and 5–7 in the gas phase the molar extinction coefficients (L mol^{-1} cm^{-1}) were directly determined through the Beer–Lambert law; the concentrations were estimated from the pressure in the IR cell, easily measured for these compounds: 1, 2073 cm^{-1} (ε 544); 5, 948 cm^{-1} (ε 55); 6, 1723 (ε 222), 1733 cm^{-1} (ε 257); 7, 912 cm^{-1} (ε 323).

For 4, the molar extinction coefficient was determined indirectly from the experimental spectrum recorded in the gas phase by Fletcher and Barish:[5] 2130 cm^{-1} (ε 593). The same value was used for 8 and for 12. Owing to the low vapor pressure of 2 and of 3, their gas-phase concentrations were estimated indirectly from the comparison of their IR spectra in the gas phase and in solution by using Hirota's formula.[25] The molar extinction coefficients were evaluated for the gas phase: 2, 2062 cm^{-1} (ε 732); 3, 2090 cm^{-1} (ε 449).

Acknowledgment. We thank the "Mission de la Recherche" and the "Conseil Régional Provence Alpes Côte d'Azur" for funds to purchase the FT IR spectrometer.

Registry No. 1, 14088-58-5; 2, 51884-33-4; 3, 3242-56-6; 4, 598-26-5.

(24) Glasstone, S. "Textbook of Physical Chemistry"; Macmillan and Co.: London, 1962; p 1075.

(25) Rao, C. N. R. "Chemical Applications of Infrared Spectroscopy"; Academic Press: New York, 1963; p 583.

Sulfonamidyls. 5. Electron Spin Resonance Spectroscopic Evidence for Four- and Five-Membered-Ring Sulfonamidyls and Sulfonyl Nitroxides

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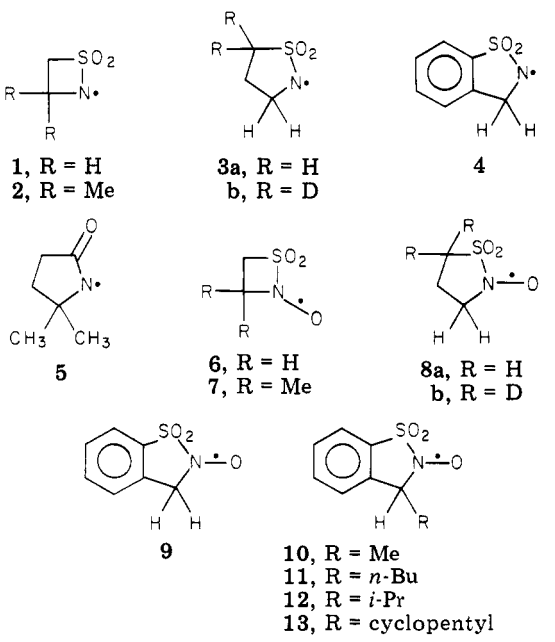
Cyclic sulfonamidyl radicals, generated by photolysis of the *N*-bromo (or *N*-chloro) β- and γ-sultams 1–3 and of *N*-bromo-2,3-dihydro-1,2-benzisothiazole 1,1-dioxide (4) have been characterized by solution ESR studies. The nitrogen and β hyperfine splitting constants of 1–4 are in agreement with a Π_N electronic ground state involving a planar geometry around the nitrogen free radical center. The corresponding nitroxides (6–9) were generated from 1–4 by reaction with nitrogen dioxide. In the same way, four additional sulfonyl nitroxides (10–13), derived from 3-alkyl-1,2-thiazoline 1,1-dioxide systems, were generated and studied by ESR. The possible geometry around the nitroxide nitrogen atom and further conformational implications are discussed.

The question of the electronic configuration of carboxamidyl (R_1CONR_2) and sulfonamidyl ($R_1SO_2NR_2$) radicals has been the subject of several recent investigations both by electron spin resonance (ESR) spectroscopic methods[1-3] as well as by ab initio MO quantum chemical calculations.[4] There is now general agreement that both types of amidyls reside in rather similar electronic ground states. However, the quantum mechanical results[1b] revealed a significant difference. Whereas the ground state of sulfonamidyls is a Π_N state well-separated from the Σ_N configuration, there is evidence that the ground state of carboxamidyls is a composite of configurations which in a planar geometry would be called Π and Σ. In particular a bent Σ_N state may contribute significantly. Recent results obtained by Ingold and co-workers[2d] are also suggestive for a tendency of the carboxamidyls to adopt a twisted geometry, involving a contribution of the Σ_N state. Furthermore, the

Chart I



(1) (a) Part 3: Teeninga, H.; Zomer, B.; Engberts, J. B. F. N. *J. Org. Chem.* **1979**, *44*, 4717. (b) Part 4: Teeninga, H.; Nieuwpoort, W. C.; Engberts, J. B. F. N. *Z. Naturforsch. B: Anorg. Chem., Org. Chem.* **1981**, *36B*, 279. (c) Part of this work has been presented at the 3rd International Symposium on Organic Radicals, Aug 31–Sept 4, 1981, Freiburg, West Germany; Abstract 3°ISOFR.

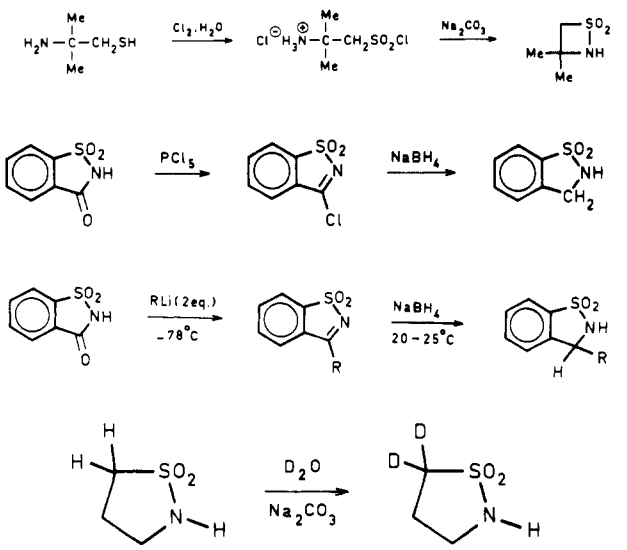
(2) Carboxamidyls: (a) Danen, W. C.; Gellert, R. W. *J. Am. Chem. Soc.* **1972**, *94*, 6853. (b) Koenig, T.; Hoobler, J. A.; Mabey, W. R. *Ibid.* **1972**, *94*, 2514. (c) Lessard, J.; Griller, D.; Ingold, K. U. *Ibid.* **1980**, *102*, 3262. (d) Sutcliffe, R.; Griller, D.; Lessard, J.; Ingold, K. U. **1981**, *103*, 624. (e) Sutcliffe, R.; Ingold, K. U.; Lessard, J. *Ibid.* **1981**, *103*, 7685.

(3) Sulfonamidyls: (a) Zomer, G.; Engberts, J. B. F. N. *Tetrahedron Lett.* **1977**, 3901. (b) Teeninga, H.; Engberts, J. B. F. N. *Recl. Trav. Chim. Pays-Bas* **1978**, *97*, 59. (c) Miura, Y.; Nakamura, Y.; Kinoshita, M. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 947. (d) Forrester, A. R.; Johansson, E. M.; Thomson, R. H. *J. Chem. Soc., Perkin Trans. 1* **1979**, 1112. (e) Danen, W. C.; Gellert, R. W. *J. Am. Chem. Soc.* **1980**, *102*, 3264. (f) Gellert, R. W. M.Sc. Thesis, Kansas State University, 1973.

(4) Carboxamidyls: (a) Baird, N. C.; Kathpal, H. B. *J. Am. Chem. Soc.* **1976**, *98*, 7532. (b) Baird, N. C.; Taylor, K. F. *Can. J. Chem.* **1980**, *58*, 733. See also ref 1b. For sulfonamidyls see 1b.

0022-3263/83/1948-0537$01.50/0

Scheme I



difference as noted above might well explain[1b] the, at first sight unexpected, higher nitrogen hyperfine splitting constants (hfsc's; A_N) for carboxamidyls than for sulfonamidyls.

Herein we describe ESR spectral data for four- and five-membered-ring sulfonamidyls and compare these results with those for the corresponding and some additional sulfonyl nitroxides. Although recently the first ESR data for a cyclic carboxamidyl were reported,[2d] the availability of more extensive data for these types of radicals would be highly desirable. However, the generation and ESR detection of cyclic carboxamidyls have appeared to be difficult,[5] probably as a result of the easy accessibility of their Σ_O states, as suggested by Koenig et al.[5b] In addition, a high chemical reactivity at the nitrogen atom of cyclic amidyls must be taken into account in view of the absence of steric protection.

Results and Discussion

The cyclic sulfonamidyls **1–4**[6] (Chart I) were generated by photolysis of carefully degassed solutions of the corresponding *N*-bromo (also *N*-chloro, for **1** and **2**) β- and γ-sultams. These precursors were prepared by halogenation of the parent β- and γ-sultams, which in turn were synthesized via the classical routes shown in Scheme I.[7] The cyclic nitroxides **6–13** were produced from the corresponding sulfonamidyls upon initially purging the solvent with nitrogen dioxide for a short time and subsequent photolysis. Interest in these sulfonyl nitroxides stems primarily from the suggestion that these radicals possess a nonplanar geometry around nitrogen.[8]

In Table I ESR data for **1–4** and **6–13** are listed, while ESR features of the corresponding acyclic radicals and the cyclic carboxamidyl **5** are given for comparison. The

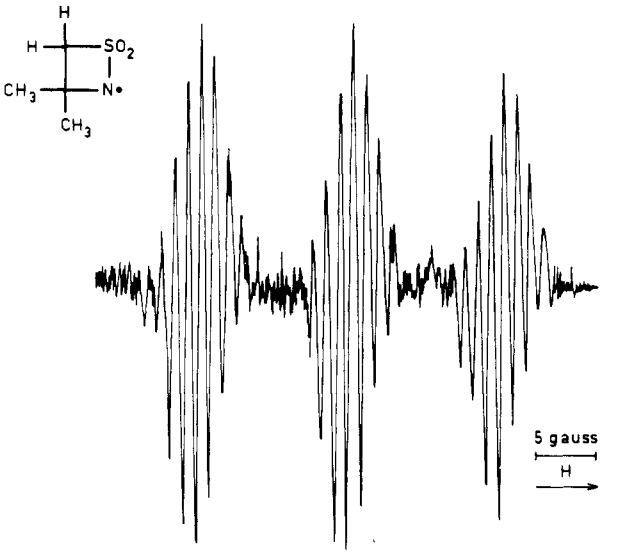


Figure 1. ESR spectrum of **2** in 3:2 (v/v) CH_2Cl_2–$CFCl_3$ at −41 °C. The two outer lines of each nitrogen line are masked by the noise.

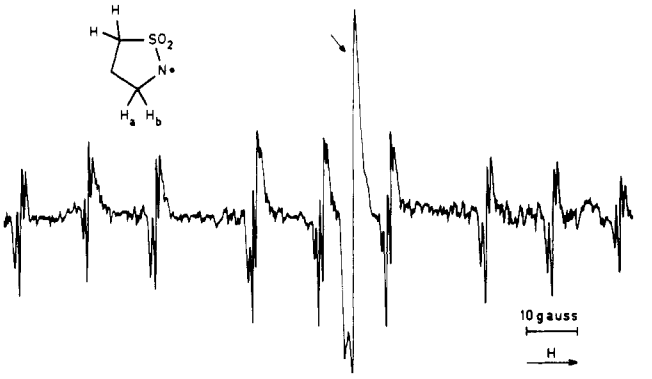


Figure 2. ESR spectrum of **3a** in 3:1 (v/v) CH_2Cl_2–$CFCl_3$ at −17 °C. A quartz absorption is indicated by an arrow.

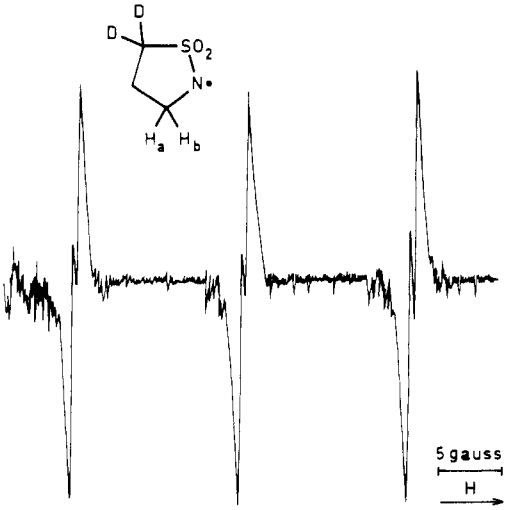


Figure 3. ESR spectrum of **3b** in 3:2 (v/v) CH_2Cl_2–$CFCl_3$ at −19 °C.

structural assignment of **1–4** and **6–13** is mainly based on the characteristic nitrogen and hydrogen hfsc's and *g* values. Thus, the ESR spectra of the β-sultam amidyls **1** and **2** (Figure 1) exhibit nitrogen hfsc's of 12.4 and 12.1 G, respectively, which are very similar to the $A_N \approx 13$ G value observed for acyclic sulfonamidyls.[3] These low A_N values indicate that the unpaired electron is contained in

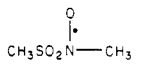
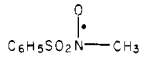
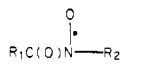
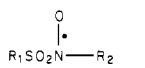
(5) (a) Danen, W. C.; Neugebauer, F. A. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 783. (b) Koenig, T.; Hoobler, J. A.; Klopfenstein, C. E.; Hedden, G.; Sunderman, F.; Russell, B. R. *J. Am. Chem. Soc.* **1974**, *96*, 4573.

(6) ESR data for **3a** have already been published by Danen and Gellert.[3e] As a consequence of the poor signal to noise ratio,[3f] the accuracy of these data is only 5%. Therefore we decided to reinvestigate this radical using the parent *N*-bromo sultam. Under these conditions we obtained a much better spectrum and different ESR data. Generally, higher steady-state concentrations of sulfonamidyls can be obtained from *N*-bromo sulfonamides than from the corresponding *N*-chloro sulfonamides.

(7) We are much indebted to Professor A. Le Berre for a generous gift of 1,1-dioxo-1,2-thiazetidine.

(8) Wajer, T. A. J. W.; Geluk, H. W.; Engberts, J. B. F. N.; de Boer, T. J. *Recl. Trav. Chim. Pays-Bas* **1970**, *89*, 696.

Table I. ESR Spectral Data[a] of Cyclic and Acyclic Carboxamidyls and Sulfonamidyls (1-5) and the Derived Nitroxides (6-13)

radical	temp, °C	A_N, G	A_{H_β}, G	A_{H_γ}, G	g	conditions
1	−40	12.4[b]	44.5 (2 H)[b]	1.4 (2 H)	2.0050	*d*
2	−20	12.1		1.03 (8 H)	2.0043	*d, e*
3a	−75	13.3	47.1 (1 H), 46.3 (1 H)	0.90 (2 H)	2.0045	*e*
	−17	13.3	46.5 (1 H), 45.6 (1 H)	0.86 (2 H)	2.0045	
3b	−31	13.3	46.6 (1 H), 45.9 (1 H)		2.0045	*e*
4	−40	13.3	45.4 (1 H), 44.8 (1 H)		2.0044	*f*
5	−53	11.2			2.0063	*g*
$CH_3SO_2\dot{N}CH_3$	−2 to −50	13.40	30.4 (3 H)	<0.2 (3 H)	2.0045	*h*
o-$MeC_6H_4SO_2\dot{N}CH_3$	−10 to −80	13.52	30.2 (3 H)		2.0044	*h*
$R_1C(O)\dot{N}R_2$		14.7-15.7			2.0044-2.0055	ref 2
$R_1SO_2\dot{N}R_2$		12.9-13.4			2.0041-2.0046	ref 3
6	−40	12.3	17.1 (2 H)	0.4 (2 H)	2.0061	*i*
7	−12	12.4		0.7 (2 H)	2.0060	*j*
8a	−60	12.0	17.2 (2 H)	1.32 (2 H)[c]		*k, l*
	−28	12.0	16.7 (2 H)	1.27 (2 H)	2.0062	
8b	−35	12.1	16.8 (2 H)		2.0061	*l*
9	−40	11.6	14.7 (2 H)		2.0061	*i*
10	−58	11.5	13.9 (1 H)		2.0063	*k*
	−10	11.8	13.7 (1 H)			
11	−77	11.2	14.2 (1 H)		2.0061	*k*
	−24	11.5	13.7 (1 H)			
12	−58	11.2	12.6 (1 H)		2.0067	*k*
	−22	11.3	12.5 (1 H)			
13	−40	11.5	11.5 (1 H)		2.0061	*i*
	−20 to −80	11.94	11.2 (3 H)	0.75 (3 H)		*l*
	−20 to −40	11.95	10.6 (3 H)			*m*
		ca. 7.5			~2.0068	ref 15
		11.0-12.0			~2.0062	ref 8

[a] The estimated accuracy of the hfsc's is usually ±0.05 G. [b] Estimated accuracy of ca. 2%. [c] When the prepared sample was carefully degassed, an additional splitting (0.37 G (2 H)) could be resolved. [d] Photolysis of a solution of the corresponding *N*-chloro sultam (0.1 M) in 3:2 (v/v) CH_2Cl_2-CCl_4. [e] Photolysis of a solution of the corresponding *N*-bromo sultam (0.1 M) in 1:2 or 1:3 (v/v) CH_2Cl_2-$CFCl_3$. [f] Same as *e*, in a 4:1 (v/v) solvent mixture. [g] See ref 2d. [h] Photolysis of a solution of the corresponding acyclic *N*-bromo sulfonamide (0.2 M) in 1:3 (v/v) CH_2Cl_2-$CFCl_3$. [i] Photolysis of a solution of the parent *N*-chloro sultam (0.2 M) in 3:2 (v/v) CH_2Cl_2-CCl_4. The solvent was initially purged with NO_2, until it developed a brown color. [j] Same as *i*, but 0.07 M sultam in 1:1 (v/v) $CFCl_3$-benzene; somewhat less NO_2 is sufficient. [k] As *i*, in 1:3 (v/v) CH_2Cl_2-$CFCl_3$. [l] Photolysis of a solution of the parent *N*-bromo sulfonamide (0.1 M) or *N*-bromo sultam in 1:3 (v/v) CH_2Cl_2-$CFCl_3$. NO_2 was added as in *i*, and the sample was freed from oxygen by means of two freeze-thaw cycles. [m] Oxidation of the parent *N*-hydroxy sulfonamide (0.01 M) with PbO_2 in 3:2 (v/v) CH_2Cl_2-CCl_4.

an orbital of distinct π character. The same conclusion holds for sulfonamidyls **3a,b** (Figures 2 and 3) and **4**. Since the difference in internuclear S–N–C bond angle between **1** (or **2**) and **3a,b** (or **4**) is most likely at least 15°, it is clear that the A_N values are only slightly dependent on this structural parameter.[9,10]

The A_N values for the acyclic and cyclic carbox- and sulfonamidyls listed in Table I reveal interesting differences. On the one hand the A_N values for the cyclic sulfonamidyls **3a,b**, and **4** (13.3 G) are higher than that for the cyclic carboxamidyl **5** (11.2 G), suggesting more spin delocalization for the latter; on the other hand, the A_N values for acyclic sulfonamidyls (13.3 G) are lower than those for acyclic carboxamidyls (14.7–15.7 G). Since a carbonyl group has usually a greater spin-delocalization capacity than a sulfonyl moiety, the observed difference between the cyclic amidyls is expected, whereas the difference for the acyclic ones is unexpected, as pointed out earlier.[1a,3a] The relatively low A_N value (11.2 G) and high g value (2.0063) of the, most likely, planar cyclic carboxamidyl **5** imply extensive spin delocalization onto the carbonyl oxygen.[2d] As was noted above, a contribution of a bent Σ_N state to the electronic ground state would lead to higher A_N values. Such a contribution would necessarily occur in a twisted conformation. On the basis of the relatively high A_N values (14.7–15.7 G) for acyclic carboxamidyls, one can reasonably conclude that these rad-

(9) A crystal structure determination[10] of the parent β-sultam of **2** provided, inter alia ∠SNC = 94.1° and ∠SNC, CNH = 51.0°, indicating the presence of a pyramidal nitrogen atom. Apparently, the hybridization of nitrogen in the β-sultam is essentially different from that in the corresponding sulfonamidyl.

(10) Van Bolhuis, F.; Teeninga, H.; Engberts, J. B. F. N., to be submitted for publication.

(11) As shown by Ingold et al.,[2d] the twisting depends strongly on the substituent attached to the nitrogen atom. This conclusion is based on the attendant variations of the A_N values (14.7–15.7 G).

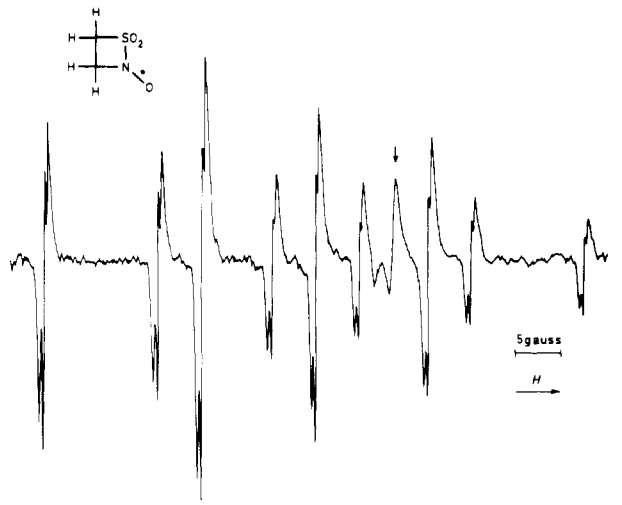


Figure 4. ESR spectrum of **6** in 3:2 (v/v) CH_2Cl_2–CCl_4 at −40 °C. A quartz absorption is indicated by an arrow. The spectrum is asymmetric, presumably as a result of the rapid decay of the radicals.

icals are partly twisted. In the absence of further model computations it cannot be decided whether the main driving force for twisting arises from the energy gain resulting from mixing of electronic states or from nonbonded interactions in the nontwisted conformation. The sulfonamidyls **1–4** can be easily distinguished from the corresponding sulfonyl nitroxides **6–9** on basis of the different g values. If β-hydrogen atoms are present, the $A_{H\beta}$ values also differ considerably. In addition, the ESR spectrum of **2** (Figure 1) is best reconcilable with eight resolvable γ-hydrogens due to both β-methyl substituents and the remaining CH_2SO_2 γ-hydrogens, whereas no β-methyl splitting is resolved in the ESR spectrum of **7**. Instead, the sulfonyl nitroxides **6–8a** show small hfsc's due to two CH_2SO_2 γ-hydrogens (see Figure 4). Similar γ-H hfsc's could be resolved for **1** and **3a**. As can be seen from Table I and in Figure 3, the CH_2SO_2 γ-H hfsc's are absent in **3b** and **8b**, which are selectively deuterated at the 5-position. At the same time deuteration of these radicals allows a correct assignment of the various γ-H hfsc's.

In the sulfonamidyls **1**, **3a**, and **4** the dihedral angle θ between the H–C–N plane and the plane defined by the N–C bond and the $2p_z$ orbital on nitrogen can be calculated by means of the Heller–McConnell equation (eq 1).[12]

$$A_{H_\beta} = \rho_N(B_0 + B_1 \langle \cos^2 \theta \rangle) \quad (1)$$

Herein B_0 and B_1 are parameters related to spin polarization and hyperconjugation, respectively, and ρ_N is the spin density in the $2p_z$ orbital on nitrogen. B_0 is usually taken to be zero, and $B_1\rho_N$ can be calculated for alkanesulfonamidyls (60.8 G) and for arenesulfonamidyls (60.4 G) by assuming a freely rotating methyl group (i.e. $\langle \cos^2 \theta \rangle = 0.5$) for the pertinent N-methyl sulfonamidyls listed in Table I. The calculated dihedral angles θ, listed in Table II, nearly match the theoretically expected value (30°). In agreement with Danen and Gellert[3e,f] and with theoretical calculations,[1b] we note that these values are readily reconcilable with a planar geometry around the nitrogen free radical center. Surprisingly, the two H_β atoms of **3a,b** (as nicely demonstrated by Figures 2 and 3) and **4** appeared to be magnetically different, indicating a slightly twisted structure. In the absence of a pronounced temperature effect the radicals must reside in a stable conformation

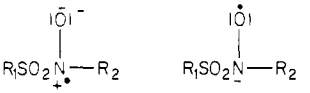
Table II. Calculated[a] Dihedral Angles θ for the Sulfonamidyls[c] 1, 3a, and 4 and the Sulfonyl Nitroxides[d] 6, 8a, and 9–13

radical	temp, °C	$A_{H\beta}$,[b] G	θ, deg
1	−40	48.1	27.2
3a	−75	47.5	27.9
		46.7	28.8
	−17	46.9	28.6
		45.9	29.7
4	−40	46.1	29.1
		45.5	29.8
6	−40	16.6	30.6
8a	−60	17.1	29.1
	−28	16.6	30.6
9	−40	15.1	32.4
10	−58	14.4	34.5
	−10	13.9	35.9
11	−77	15.2	32.1
	−24	14.2	35.1
12	−58	13.4	37.3
	−22	13.2	37.9
13	−40	12.0	41.2

[a] See text. [b] Small corrections were applied to correct for the increase or the decrease in A_N with respect to the A_N values of the N-methyl-substituted radicals. [c] Estimated accuracy of ±0.5°. [d] Estimated accuracy from ±0.8° for **6** to ±0.5° for **13**.

within the employed temperature range. The slight decrease in A_{H_β} of **3a** with increasing temperature can therefore be ascribed to oscillations[13] around the equilibrium values of the dihedral angle θ.

Previously it has been suggested that sulfonyl nitroxides possess a nonplanar geometry around the nitroxide nitrogen atom.[3d,8,14] This suggestion was largely based on the observation that the A_N values (ca. 11.5 G) are much higher than those of structurally related acyl nitroxides (ca. 7.5 G, Table I). It was anticipated that resonance structure A would be greatly destabilized relative to B as



A B

a result of the strong electron-attracting properties of the sulfonyl moiety. This would lead to a reduced spin density at nitrogen. It was assumed that delocalization of the unpaired electron onto the sulfonyl group can be neglected. Recent ^{17}O-labeling studies[15,16] provide strong support for this assumption. The Heller–McConnell equation (eq 1) can be also applied to **6**, **8a**, and **9** to derive a value for the dihedral angle θ, as defined above for the sulfonamidyls. By taking $B_0 = 0$ and $B_1\rho_N = 22.4$ and 21.2 G for alkyl and aryl systems, respectively, we calculate angles of about 30°[17] (see Table II), thereby providing evidence against the possibility of a bent nitrogen atom in sulfonyl nitroxides. This then implies that the difference in A_N between sulfonyl and acyl nitroxides should be primarily explained in terms of spin-delocalization onto the carbonyl group of the latter.[15]

(12) Janzen, E. G.; Allinger, N. L.; Eliel, E. L., *Top. Stereochem.* **1971**, *6*, 177.

(13) See for example: Stone, E. W.; Maki, A. H. *J. Chem. Phys.* **1962**, *37*, 1326.

(14) Rawson, G.; Engberts, J. B. F. N. *Tetrahedron* **1970**, *26*, 5653.

(15) Aurich, H. G.; Czepluch, H. *Tetrahedron* **1980**, *36*, 3543.

(16) Compare ref 3a and: Norman, R. O. C.; Carton, P. M.; Gilbert, B. C.; Laue, H. A. H.; Sealy, R. C. *J. Chem. Soc., Perkin Trans. 2* **1975**, 1245.

(17) With respect to the calculated θ of about 33° for **9**, we note that a (slight) ring pucker at CH_2 in the five-membered ring of this radical will increase θ.

Table II also shows the calculated dihedral angles of the thiazoline nitroxide systems **10–13**, based on the A_{H_β} values for the methine hydrogen atoms. They reveal some puckering at CH–R in the five-membered ring of these radicals, the effect becoming more pronounced with the more bulky R group.

Although it has not been definitely established that **10–13** reside in a single conformation in the examined temperature range, the moderate effect of temperature on the A_{H_β} hfsc's makes this a reasonable interpretation. Unfortunately, the method used for the generation of the radicals does not allow ESR studies over a wider temperature range.[18]

Experimental Section

Melting points were determined on a Mettler FP2 apparatus. ^{1}H NMR spectra were obtained on a 60-MHz Hitachi Perkin-Elmer R24B spectrometer. Chemical shifts (δ) are downfield from Me_4Si. Infrared spectra were recorded on a Unicam SP 200 spectrophotometer and ultraviolet spectra on a Cary 210 spectrophotometer. Mass spectra were determined by Mr. A. Kiewiet on an AEI MS 902 apparatus. ESR spectra were recorded on a Varian E-4 apparatus fitted with a Varian A-1268 variable-temperature controller (checked with a copper–constantan thermocouple). The spectra of the sulfonamidyls were determined by using solutions totally freed from dissolved oxygen by at least four freeze–thaw cycles using a high-vacuum technique at pressures below 10^{-5} torr. Photolyses were carried out by using a Philips SP-500-W lamp for *N*-bromo sultams and a Philips SP-500-WQ lamp for *N*-chloro sultams. Best results were obtained by focusing the light on the ESR cavity by means of a lens system. The *g* values (±0.0002) were measured by employing diphenylpicrylhydrazyl (DPPH) as a reference compound (g = 2.0037).

The following compounds were synthesized by following literature procedures: *tert*-butyl hypobromite,[19] *tert*-butyl hypochlorite,[20] pseudosaccharin chloride,[21] 2-amino-2-methylpropane-1-thiol[22] (from 2,2-dimethylaziridine[23]), propane sultam,[24] and 3-methyl- and 3-*n*-butyl-1,2-benzisothiazole 1,1-dioxide.[25]

The purity of the *N*-halo sulfonamides used in the photolyses was assumed to be ≥95% since no parent sulfonamide could be detected by NMR and IR spectroscopy.

***N*-Chloroethanesultam.** *tert*-Butyl hypochlorite (0.22 g, 0.002 mol) was added dropwise at 0 °C to a solution of ethanesultam[7,26] (0.2 g, 0.0019 mol) in 35 mL of dichloromethane. After being stirred in the dark at 0 °C for 7 h the solution was washed with 4 mL of ice–water. The organic layer was dried ($MgSO_4$), and the solvent was removed in vacuo at a temperature below 10 °C: yield 0.24 g (91%); mp 71.8–73.8 °C; NMR ($CDCl_3$) δ 3.52 (t, 2 H), 4.28 (t, 2 H); IR (KBr) 3030, 1350, 1330, 1200, 1167, 800 cm^{-1}.

2-Amino-2-methylpropanesulfonyl Chloride (HCl Salt). For 1 h chlorine gas was bubbled through a solution of 2-amino-2-methylpropane-1-thiol (2.20 g, 0.021 mol) and H_2O (0.38 g, 1 equiv) in 50 mL of MeOH. The temperature was kept between 0 and 4 °C. Evaporation of the solvent in vacuo at room temperature gave the crude, hygroscopic product in an almost quantitative yield: NMR (MeOH-d_4) δ 1.63 (s, 6 H), 4.52 (s, 2 H); IR (KBr) 3000 (br), 1380, 1180 cm^{-1}. This material was cyclized without further purification.

1,1-Dioxo-3,3-dimethyl-1,2-thiazetidine (3,3-Dimethylethanesultam). This compound was prepared by a procedure similar to that given by Le Berre.[26] A solution of Na_2CO_3 (2.07 g, 0.02 mol) in water (12 mL) was added dropwise at 0 °C for 10 min to a stirred solution of the HCl salt of 2-amino-2-methylpropanesulfonyl chloride (2.0 g, 0.01 mol) in a mixture of $CHCl_3$ (100 mL) and water (10 mL). After the mixture was stirred for 45 min at 0–5 °C, the organic layer was separated, and the aqueous layer was extracted with 50 mL of $CHCl_3$. The combined chloroform layers were washed with water (10 mL) and were dried ($MgSO_4$). Evaporation of the solvent gave an oil (1.0 g, 74%) which was pure β-sultam according to NMR spectroscopy. Crystallization from ether–*n*-pentane gave 0.45 g (33%) of the pure material: mp 35.5–37.5 °C; NMR ($CDCl_3$) δ 1.57 (s, 6 H), 3.93 (s, 2 H), 5.1–5.6 (br s, 1 H); IR (KBr) 3380, 1320, 1215, 1135 cm^{-1}; MS, *m/e* (relative intensity) 135 (M^+), 56 ($M^+ - MeSO_2$, 100). Anal. Calcd for $C_4H_9NO_2S$: C, 35.54; H, 6.71; N, 10.36; S, 23.72. Found: C, 35.59; H, 6.70; N, 10.45; S, 23.76.

***N*-Bromo-3,3-dimethylethanesultam.** *tert*-Butyl hypobromite (0.14 g, 0.000 92 mol) in 1 mL of dichloromethane was added dropwise to a solution of the β-sultam (0.112 g, 0.000 83 mol) in 4 mL of dichloromethane. After the mixture was stirred in the dark at 0 °C for 2.5 h, 5 mL of dichloromethane was added, and the solution was washed with 4 mL of 0.2 N NaOH and 4 mL of ice–water. The organic layer was dried ($MgSO_4$), and the solvent was removed in vacuo at a temperature below 10 °C. Then a small amount of trichlorofluoromethane was added, and the evaporation process was repeated. This afforded the pale yellow *N*-bromo β-sultam: 0.16 g (90%); mp 73–76 °C; UV (CH_2Cl_2) λ_{max} 296 nm (ϵ 240); NMR ($CDCl_3$) δ 1.51 (s, 6 H), 4.07 (s, 2 H); IR (KBr) 2955 (s), 1310, 1195 cm^{-1}; MS, *m/e* (relative intensity) 213, 215 (M^+), 120 ($M^+ - CH_2Br$, 100).

2,3-Dihydro-1,2-benzisothiazole 1,1-Dioxide. Sodium borohydride (4.1 g, 0.108 mol) was added in small portions to a solution of pseudosaccharin chloride (5.0 g, 0.027 mol) in freshly distilled THF (150 mL) at 0 °C. After the mixture was stirred for 24 h at room temperature, water (15 mL) was added under cooling. The solvent was evaporated in vacuo at 20 °C, and the mixture was further hydrolyzed with 4 N HCl until pH 4. The aqueous layer was extracted once with 100 mL of chloroform and three times with 50 mL of chloroform. The combined organic layers were dried ($MgSO_4$), and the solvent was evaporated. The remaining crude product (2.93 g, 64%) was crystallized from 1:9 (v/v) EtOH–H_2O or from EtOH–CCl_4: mp 110–112 °C (lit.[27] mp 111–113 °C); NMR (acetone-d_6) δ 4.55 (s, 2 H), 6.45 (br s, 1 H), 7.3–7.55 (m, 4 H); IR (KBr) 3300, 1410, 1300, 1170, 760 cm^{-1}; MS, *m/e* (relative intensity) 169 (M^+, 100).

***N*-Chloro-2,3-dihydro-1,2-benzisothiazole 1,1-Dioxide.** *tert*-Butyl hypochlorite (0.48 g, 0.0044 mol) was added dropwise to a solution of the benzyl sultam (0.40 g, 0.0024 mol) in 20 mL of dry methanol. After the mixture was stirred for 2.5 h at 0 °C in the dark, the solvent was removed in vacuo at ca. 10 °C. The residue was dissolved in 40 mL of cold chloroform, and the solution was washed with 4 mL of ice–water. After the organic layer was dried ($MgSO_4$), the solvent was evaporated in vacuo at 10 °C: yield 0.49 g (100%); mp 82–86 °C dec; NMR ($CDCl_3$) δ 4.58 (s, 2 H), 7.18–7.90 (m, 4 H); IR (KBr) 1460, 1330, 1170, 760 cm^{-1}; UV (EtOH) λ_{max} 266 nm (ϵ 1050).

***N*-Bromo-2,3-dihydro-1,2-benzisothiazole 1,1-Dioxide.** A solution of bromine (0.23 mL, 0.0045 mol) in 1 N NaOH (11 mL) was added dropwise at 0 °C during 10 min to a solution of the benzyl sultam (0.385 g, 0.0023 mol) in 12 mL of chloroform. After the mixture was stirred in the dark for 2.5 h at 0 °C, the organic layer was separated and washed with 4 mL of ice–water. Each aqueous layer was extracted with 5 mL of chloroform. The combined chloroform layers were dried over $MgSO_4$ at −20 °C. Then the solvent was removed in vacuo at 0 °C in the dark. A small amount of trichlorofluoromethane was then added and evaporated at 0 °C. The yellow *N*-bromobenzyl sultam (0.3 g, 53%) decomposed rather rapidly at 20 °C: UV (EtOH) λ_{max} 255

(18) This is due to the poor solubility of the parent *N*-chloro sultams at low temperatures. In addition, less NO_2 will be present at lower temperatures because the equilibrium $N_2O_4 \rightleftharpoons 2NO_2$ is shifted to the left. At higher temperatures the initially generated sulfonamidyls are more likely to decompose than to be oxidized by NO_2.

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nm (ε 1600), 298 (800); NMR ($CDCl_3$) δ 4.50 (s, 2 H), 7.3–7.8 (m, 4 H); IR (KBr) 1165, 1315 cm^{-1}.

5,5-Dideuteriopropanesultam. A solution containing propanesultam (0.7 g, 0.0058 mol), sodium carbonate (1.23 g, 0.012 mol), and D_2O (9 mL) was refluxed for 18 h. The solution was cooled, and acidified until pH 2 with 5 N DCl, and extracted five times with 10 mL of dichloromethane. The combined organic layers were dried (Na_2SO_4), and the solvent was evaporated. This afforded a colorless oil (0.47 g, 66%) which was purified by Kugelrohr distillation (120 °C, 0.02 mm): NMR ($CDCl_3$) δ 2.4 (t, 2 H), 3.38 (t, 2 H), 4.8 (br s, 1 H); IR (neat) 3350, 2500, 1310, 1160 cm^{-1}; MS, *m/e* (relative intensity) 123 (M^+, 100); exact mass calcd for $C_3D_2H_5NO_2S$ 123.031, found 123.032.

3-Isopropyl-1,2-benzisothiazole 1,1-dioxide was obtained as one of the decomposition products of *N*-bromo-3,3-diisopropyl-1,2-benzisothiazoline 1,1-dioxide: NMR ($CDCl_3$) δ 1.40 (d, 6 H), 3.38 (heptet, 1 H), 7.52–7.97 (m, 4 H); IR (KBr) 2970, 1560, 1340, 1170, 810 cm^{-1}; exact mass calcd for $C_{10}H_{11}NO_2S$ 209.051, found 209.050.

3-Alkyl-1,2-benzisothiazoline 1,1-Dioxides. In a typical example, sodium borohydride (0.17 g, 0.0045 mol) was added in small portions to a stirred solution of the appropriate thiazole (0.0011 mol) in anhydrous ether (30 mL). Then ethanol (20 mL) was added, and the resulting solution was stirred for 24 h at room temperature. After addition of 4 N HCl (3 mL) the organic solvents were removed in vacuo, and, after addition of chloroform (15 mL), the mixture was further hydrolyzed with 4 N HCl until pH 2. The organic layer was separated, and the aqueous layer was extracted with two portions of chloroform (15 mL). The combined organic layers were dried ($MgSO_4$), and the solvent was evaporated. The residue was purified by crystallization and/or preparative layer chromatography (PLC).

3-Methyl-1,2-benzisothiazoline 1,1-Dioxide. After purification by PLC (SiO_2, ether) this compound was obtained in a yield of 40% as a colorless oil, which crystallized very slowly: NMR ($CDCl_3$) δ 1.55 (d, 3 H), 4.73 (m, 1 H), 5.25 (br s, 1 H), 7.2–7.8 (m, 4 H); IR (neat) 3300, 1295, 1170, 760 cm^{-1}; exact mass calcd for $C_8H_9NO_2S$ 182.966, found 182.965.

3-*n*-Butyl-1,2-benzisothiazoline 1,1-Dioxide. This compound was purified by PLC (SiO_2, ether) and recrystallized from 1:4 (v/v) benzene–*n*-hexane: yield 75%; mp 63–64 °C; NMR ($CDCl_3$) δ 0.65–2.20 (m, 9 H), 4.65 (dd, 1 H) 5.27 (d, 1 H) 7.2–7.8 (m, 4 H); IR (neat) 3300, 2960, 1480, 1400, 1300, 1175, 1140, 765 cm^{-1}; exact mass calcd for $C_{11}H_{15}NO_2S$ 225.082, found 225.083.

3-Isopropyl-1,2-benzisothiazoline 1,1-Dioxide. Obtained as a colorless oil: yield 67% [from 1:3 (v/v) benzene–*n*-hexane]; NMR ($CDCl_3$) δ 0.75 (d, 3 H), 1.10 (d, 3 H), 2.0–2.5 (m, 1 H), 4.65 (dd, 1 H), 5.35 (br d, 1 H), 7.2–7.85 (m, 4 H); IR (neat) 3300, 2970, 1480, 1300, 1170, 765 cm^{-1}; exact mass calcd for $C_{10}H_{13}NO_2S$ 211.067, found 211.068.

3-Cyclopentyl-1,2-benzisothiazoline 1,1-Dioxide. This compound was obtained during an attempt to synthesize the corresponding dicyclopentyl system by following the route of Mustafa.[28] Purification of the yellow oil by acid–base separation, column chromatography (neutral Al_2O_3, ether, R_f ~0.6; the column was eluted with an increasing amount of ethyl acetate) and crystallization from benzene–petroleum ether (60:80) afforded the product in low yield (6%): mp 82–84 °C; NMR ($CDCl_3$) δ 1.1–2.6 (m, 9 H), 4.62 (dd, 1 H), 5.05 (br s, 1 H), 7.1–7.8 (m, 4 H); IR (KBr) 3300, 2960, 1460, 1400, 1290, 1170, 760 cm^{-1}; MS, *m/e* (relative intensity) 237 (M^+), 168 ($M^+ - C_5H_9$, 100). Anal. Calcd for $C_{12}H_{15}NO_2S$: C, 60.37; H, 6.37; N, 5.90. Found: C, 60.18; H, 6.56; N, 5.73. The remaining N-brominations and N-chlorinations were carried out by following the method given for 2-bromo-3,3-dimethylethanesultam and *N*-chlorobenzyl sultam, respectively, except for *N*-chloro-3,3-dimethylethanesultam, which was prepared in the same way as *N*-chloroethanesultam.

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Registry No. **1**, 84108-76-9; **2**, 84108-77-0; **3a**, 74387-90-9; **3b**, 84108-78-1; **4**, 84108-79-2; **5**, 76826-98-7; **6**, 84108-81-6; **7**, 84108-82-7; **8a**, 84108-83-8; **8b**, 84108-84-9; **9**, 84108-85-0; **10**, 84117-44-2; **11**, 84108-86-1; **12**, 84108-87-2; **13**, 84108-88-3; $CH_3SO_2NCH_3$, 74387-87-4; *o*-$MeC_6H_4SO_2NCH_3$, 84108-80-5; $CH_3SO_2N(O)CH_3$, 27653-90-3; $C_6H_5SO_2N(O)CH_3$, 84109-02-4; *tert*-butyl hypochlorite, 507-40-4; ethanesultam, 34817-61-3; *N*-chloroethanesultam, 84108-89-4; 2-amino-2-methylpropane-1-thiol, 13893-24-8; 2-amino-2-methylpropanesulfonyl chloride hydrochloride, 84108-90-7; *tert*-butyl hypobromite, 1611-82-1; 3,3-dimethylethanesultam, 84108-91-8; *N*-bromo-3,3-dimethylethanesultam, 84108-92-9; 2,3-dihydro-1,2-benzisothiazole 1,1-dioxide, 936-16-3; pseudosaccharin chloride, 567-19-1; *N*-chloro-2,3-dihydro-1,2-benzisothiazole 1,1-dioxide, 84108-93-0; *N*-bromo-2,3-dihydro-1,2-benzisothiazole 1,1-dioxide, 84108-94-1; propanesultam, 5908-62-3; 5,5-dideuteriopropanesultam, 84108-95-2; *N*-bromo-3,3-diisopropyl-1,2-benzisothiazoline 1,1-dioxide, 84108-96-3; 3-isopropyl-1,2-benzisothiazole 1,1-dioxide, 84108-97-4; 3-methyl-1,2-benzisothiazoline 1,1-dioxide, 84108-98-5; 3-*n*-butyl-1,2-benzisothiazoline 1,1-dioxide, 84108-99-6; 3-isopropyl-1,2-benzisothiazoline 1,1-dioxide, 84109-00-2; 3-cyclopentyl-1,2-benzisothiazoline 1,1-dioxide, 84109-01-3.

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Quenching of Singlet Oxygen by 1,3,5-Triaryl-2-pyrazolines

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The efficient quenching of photochemically generated singlet oxygen by four 1,3,5-triaryl-2-pyrazolines (**5–8**) and *p*-(diethylamino)benzaldehyde diphenylhydrazone (**9**) has been investigated by inhibition of the photosensitized oxygenation of 1,3-diphenylisobenzofuran and 2-methyl-2-pentene. 1-Phenyl-3-[*p*-(diethylamino)styryl]-5-[*p*-(diethylamino)phenyl]-2-pyrazoline (**8**) quenches singlet oxygen without any reaction at all, and the quenching rate constant reaches a maximum of 5.8×10^9 M^{-1} s^{-1}. The quenching ability correlates with the value of their one-electron oxidation potentials (E_p).

It is well-known that singlet oxygen is an active oxygen species and that it may be involved in photodegradation of cells by pigments, light, and oxygen in biological systems.[1] Efficient quenchers of $^1O_2$[2] might, therefore, have practical importance. Carotenes,[3] the most efficient quenchers, show protective action against photobleaching

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