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Azabrendanes. I. Synthesis, Structure and Spectral Parameters of N-(Arylsulfonyl)-Exo-2-hydroxy-4-azatricyclo[4.2.1.$0^{3,7}$]nonanes

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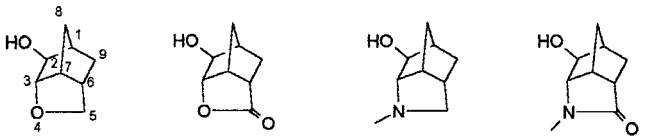
ABSTRACT

A number of N-(arylsulfonyl)bicyclo[2.2.1]hept-2-en-endo-5-methylamines have been synthesized from bicyclo[2.2.1]hept-2-en-endo-5-carbonitrile via reduction of the latter by lithium aluminum hydride and subsequent reactions of the resulting amine with arylsufonyl chlorides. The structures and stereochemical homogeneity of the products have been supported by the analysis of ^{1}H NMR spectra and by COSY-experiments. The reactions of the sulfonamides with peroxyphthalic acid are accompanied by intramolecular cyclizations and are completed by the formation of N-(arylsulfonyl)-exo-2-hydroxy-4-azatricyclo[4.2.1.$0^{3,7}$]nonanes. The structures of the substituted azabrendanes have been confirmed by spectral methods. The molecular structure of N-(p-methoxycarbonylaminophenylsulfonyl)-exo-2-hydroxy-4-azatricyclo[4.2.1.$0^{3,7}$]nonane **8j** *has been determined by X-ray diffraction analysis. © 1997 John Wiley & Sons, Inc.*

INTRODUCTION

Tricyclic structures (**1–4**) are of interest as potential biologically active systems or as synthons for their preparation.



1 **2** **3** **4**

Among them, hydroxyethers of type **1** and lactones of type **2**, which are easily obtained by epoxidation of the substituted norbornenes having endo-orientation of oxygen-containing substituents, i.e., hydroxymethyl [1] and carboxyl [2] groups, are known best. Ring transformations of this kind are attributed to favorable location of a nucleophilic group in the vicinity of the loosening π^*-molecular orbital of the incipient epoxy ring [3]. No nitrogen-containing structures (**3**,**4**) have been observed in such epoxidation reactions. Epoxidation of endo-carboxamides of the norbornene series is completed with the formation of lactones of type (**2**) [4]. Intramolecular rear attack by the oxygen of the carbonyl group at the electrophilic site in the intermediate of the olefin-peroxyacid reaction is the key feature of the process [4].

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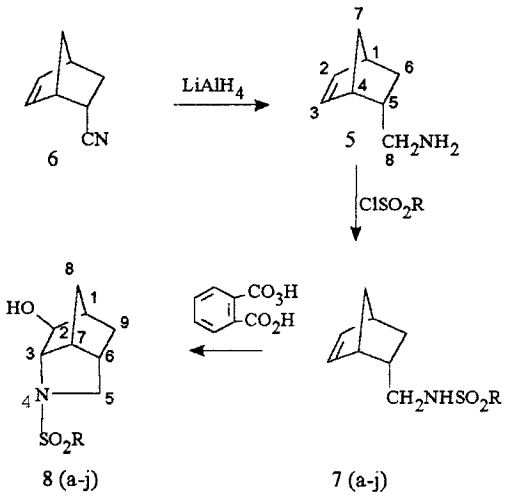
Epoxidation of amines of the norbornene series has not been given any special attention, and this is the reason why 4-azatricyclo [4.2.1.$0^{3,7}$]nonanes of type **3** are so rarely found in the literature. It is reported in Ref. [5] that only the products of amino group transformation were found among the products of oxidation of bicyclo[2.2.1]hept-2-en-endo-5-methylamine (**5**) by oxaziridines, and there were no compounds found with structures of type (**3**).

RESULTS AND DISCUSSION. CHEMICAL AND SPECTRAL INVESTIGATIONS

Nitrogen-containing polycyclic structures of type **3** have now been show to be formed in the reactions of peroxyphthalic acid with *N*-(arylsulfonyl)bicyclo[2.2.1]hept-2-en-endo-5-methylamines (**7a–j**).



8 (a-j) 7 (a-j)

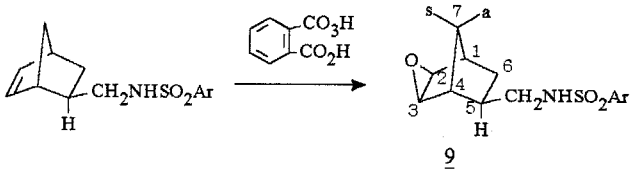
R= C_6H_5 (a); $C_6H_4CH_3$-p (b); C_6H_2(i-Pr)3-o,o',p (c); C_6H_4COOEt-p (d); C_6H_4Br-p (e); C_6H_4Cl-p (f); C_6H_4F-p (g); $C_6H_4NO_2$-p (h); $C_6H_3NO_2$-o,Cl-p (i); $C_6H_4NHCOOCH_3$-p (j)

Stereochemically homogeneous endo-sulfonamides (**7a–j**) have been obtained from bicyclo-[2.2.1]hept-2-en-endo-5-carbonitrile (**6**), isolable by fractional distillation from the mixture of products obtained by the diene synthesis of cyclopentadiene with acrylonitrile and converted into amine (**5**) by the action of lithium aluminum hydride [6]. In accordance with the literature [7] the reduction is accompanied by epimerization; the presence of an impurity (~5%) of the corresponding exo-stereoisomer has been revealed by the ^{1}H NMR spectrum. A number of sulfonamides (**7a–j**) have been obtained from the amine (**5**) by the action of aromatic sulfonylchlorides; high product yields have been achieved when the reaction was carried out in heterogeneous medium and with an equimolar ratio of the reagents. The properties of the sulfonamides (**7a–e**) have been described elsewhere [8,9] [see Table 1 for compounds (**7f–j**)]. There are biologically active sulfonamides (i.e., **7f**, **7h**, and **7i**) among those synthesized; e.g., *N*-(*p*-nitrophenylsulfonyl)bicyclo[2.2.1]hept-2-en-endo-5-methylamine (i.e., **7h**) has exhibited analgetic, anticonvulsive, and tranquilizing effects [10].

Only poor structural information can be obtained from IR spectra in studies of sulfonamides. This is primarily due to the presence of two unsaturated fragments; i.e., the double bond and the benzene ring (Table 1). The sulfonamide group is identified by the presence of intensive absorption in the regions 1350–1320, 1170–1150, and 3350–3250 cm^{-1}.

The presence of an endo-configuration of the substituents in sulfonamides (**7f–j**) can be seen distinctly by use of ^{1}H NMR spectra. The analysis of the spectra of sulfonamides (**7a–e**) and those of the corresponding exo-stereoisomers made previously have permitted us to formulate criteria for stereochemical assignments of a number of sulfonamides of the norbornene series [9,11]. The signals were assigned by comparison with the ^{1}H NMR spectrum of the initial amine (**5**), for which a two-dimensional spectrum was obtained using the COSY technique. The multiplets (*d* of *d*) of the olefinic protons (H^2, H^3), the unresolved proton multiplets at the heads of the bridge (H^1, H^4), and three systems of geminal protons at C^6, C^7, and C^8 (Table 2) are characteristic of the spectra. The first of these, in which the proton H^6 endo is additionally shielded by the magnetoanisotropic outer C^5–C^8 bond and resonates in the region of δ = 0.38–0.43, with $\Delta\delta$ (H^xH^n) exceeding 1.3 ppm, is of particular interest. It should be noted that, in the case of exo-isomers, the $\Delta\delta$ value does not exceed 0.2–0.3 ppm, and this difference, along with the other proposed criteria [9], may be used in the analysis of the PMR spectra, not only for sulfonamides, but also for other substituted norbornenes as well [12].

Earlier, we showed that epoxidation of sulfonamides of the norbornene series having the exo-configuration of the substituent with peroxyphthalic acid was completed with the formation of epoxides [9,13].



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The reaction of endo-sulfonamides (**7a–j**) with peroxyphthalic acid yielded the compounds having

TABLE 1 *N*-(Arylsulfonyl)bicyclo[2.2.1]hept-2-en-endo-5-methylamines

Compound	Mp(°C) (Yield %)	Formula	Anal. % Calcd/Found C	H	N	IR Spectral Parameters
7f	111–112 (98)	$C_{14}H_{16}ClNO_2S$	56.47 56.48	5.38 5.47	4.71 5.03	3250, 3082, 3052, 1587, 1567, 1480, 1326, 1148, 740, 713
7g	137–138 (79)	$C_{14}H_{16}FNO_2S$	59.79 59.67	5.69 5.87	4.98 5.01	3247, 3080, 3053, 1595, 1573, 1490, 1320, 1153, 713
7h	142–143 (82)	$C_{14}H_{16}N_2O_4S$	54.50 54.39	5.19 5.20	9.09 8.98	3307, 3093, 3047, 1595, 1580, 1520, 1347, 1160, 840, 733
7i	100–101 (64)	$C_{14}H_{15}ClN_2O_4S$	49.05 49.09	4.41 4.39	8.17 8.22	3352, 3096, 1560, 1440, 1320, 1168, 832, 720
7j	205–206 (96)	$C_{16}H_{20}N_2O_4S$	57.14 57.04	5.97 6.01	4.17 4.14	3368, 3264, 3062, 1728, 1440, 1324, 1236, 1152, 836, 720

TABLE 2 ^{1}H NMR ($CDCl_3$) of Compounds **7f–j** (δ/*J* Hz)

Compound	H^1	H^2	H^3	H^4	H^5	H^{6x}	H^{6n}	H^{7s}	H^{7a}	H^{8A}	H^{8B}	NH	H^{Ar}
7f	2.73	6.05 $^3J_{2,3}$5.8 $^3J_{2,1}$3.0	5.72 $^3J_{3,4}$2.8	2.74	2.10	1.72 $^2J_{6x,6n}$11.7 $^3J_{6x,5}$8.8 $^3J_{6x,1}$4.2	0.39 $^3J_{6n,5}$4.1 $^4J_{6n,7s}$2.1	1.36 $^2J_{7s,7a}$8.2 $^3J_{7s,4}$4.0	1.13	2.60	2.60	4.87	7.74, 7.43
7g	2.70	6.04	5.70	2.75	2.10	1.72 $^2J_{6x,6n}$11.5 $^3J_{6x,5}$9.1 $^3J_{6x,1}$3.8	0.38 $^3J_{6n,5}$4.1 $^4J_{6n,7s}$2.6	1.36 $^2J_{7s,7a}$8.4 $^3J_{7s,4}$4.2	1.13	2.59 $^2J_{8A,8B}$11.8	2.48	4.82	7.83, 7.17
7h	2.75	6.08 $^3J_{2,3}$5.8 $^3J_{2,1}$3.0	5.73 $^3J_{3,4}$2.8	2.73	2.12	1.74 $^2J_{6x,6n}$11.8 $^3J_{6x,5}$8.9 $^3J_{6x,1}$3.8	0.40 $^3J_{6n,5}$4.0 $^4J_{6n,7s}$2.6	1.38 $^2J_{7s,7a}$8.4 $^3J_{7s,4}$4.2	1.15	2.67 $^2J_{8A,8B}$12.6	2.58	4.79	8.31, 7.98
7i	2.75	6.09 $^3J_{2,3}$5.7 $^3J_{2,1}$2.8	5.77 $^3J_{3,4}$2.8	2.81	2.18	1.77 $^2J_{6x,6n}$11.7 $^3J_{6x,5}$9.0 $^3J_{6x,1}$3.8	0.43 $^3J_{6n,5}$4.0 $^4J_{6n,7s}$2.4	1.39 $^2J_{7s,7a}$8.4 $^3J_{7s,4}$4.0	1.17	2.69 $^2J_{8A,8B}$11.8	2.63	5.14	7.99, 8.03, 7.64
7j	2.70	6.04 $^3J_{3,2}$5.9 $^3J_{2,1}$2.9	5.71 $^3J_{3,4}$3.1	2.74	2.10	1.73 $^2J_{6x,6n}$11.7 $^3J_{6x,5}$9.0 $^3J_{6x,1}$3.8	0.39 $^3J_{6n,5}$4.0 $^4J_{6n,7s}$2.4	1.36 $^2J_{7s,7a}$8.4 $^3J_{7s,4}$4.2	1.13	2.60 $^2J_{8A,8B}$13.5	2.50	4.40	7.72, 7.47

the properties listed in Table 3. The highest yield of compound (**8b**) was obtained using crystalline peroxyphthalic acid; alternatively, the latter may be used in situ, with a decrease in hydrogen peroxide concentration (from 60 to 20%) not changing the direction of the process, but lowering the product yield. Also, with use of compound (**8b**), the dependence of the product yield and the reaction time on the ratio of olefin to oxidant was examined. When the ratio of the reagents was 1:1.5, 1:2, and 1:3.5, the product yields were 44.1, 51.3, and 82.3%, respectively. When using crystalline monoperoxyphthalic acid (75–85%), the use of a 50% oxidant excess brought about a 95.5% yield of the product. The direction of sulfonamides transformation (i.e., from the electron-accepting nitro group to the electron donor methyl and isopropyl groups in the ortho- and para positions of the benzene ring) does not depend on the nature of the substituent present in the benzene ring. The last example, i.e., the preparation of tricyclic sulfonamide (**8c**), indicates that the increased bulk of the substituent at the nitrogen and the growth of steric hindrance do not impede the course of intramolecular cyclization.

The problem of the structure of the reaction products (i.e., epoxide **9** or tricyclic sulfonamide **8**)

TABLE 3 *N*-(Arylsulfonyl)-exo-2-hydroxy-4-azatricyclo[4.2.1.$0^{3,7}$]nonanes

Compound	Mp(°C) (Yield %)	Formula	Anal. % Calcd/Found C	H	N	IR Spectral Parameters
8a	138–139 (75)	$C_{14}H_{17}NO_3S$	60.22 60.19	6.10 6.14	5.04 5.01	3446, 3050, 1606, 1470, 1444, 1328, 1160, 838
8b	70–71 (95)	$C_{15}H_{19}NO_3S$	61.35 61.41	6.54 6.53	5.01 4.77	3450, 3010, 1595, 1494, 1450, 1340, 1158, 840
8c	160–161 (91)	$C_{23}H_{35}NO_3S$	63.05 63.13	8.21 8.06	3.07 3.20	3296, 3046, 1608, 1464, 1328, 1152, 848
8d	90–91 (94)	$C_{17}H_{21}NO_5S$	58.01 58.10	6.07 6.02	4.01 3.99	3450, 3080, 1702, 1596, 1462, 1336, 1164, 838
8e	138–139 (85)	$C_{14}H_{16}BrNO_3S$	46.90 46.93	4.52 4.50	3.94 3.91	3488, 1584, 1545, 1328, 1168, 816
8f	109–110 (84)	$C_{14}H_{16}ClNO_3S$	53.56 53.58	5.17 5.14	4.49 4.46	3512, 3095, 1584, 1336, 1164, 836
8g	67–68 (94)	$C_{14}H_{16}FNO_3S$	56.50 56.55	5.45 5.42	4.73 4.71	3380, 3090, 3052, 1584, 1440, 1318, 1140, 838
8h	152–153 (88)	$C_{14}H_{16}N_2O_5S$	51.60 51.84	4.99 4.97	8.54 8.63	3530, 3090, 1593, 1513, 1340, 1153, 840, 828
8i	123–124 (93)	$C_{14}H_{15}ClN_2O_5S$	46.84 46.86	4.24 4.21	7.43 7.31	3536, 3105, 1552, 1472, 1376, 1335, 1168, 843
8j	198–199 (96)	$C_{16}H_{20}N_2O_5S$	55.07 54.93	6.05 5.92	8.03 7.99	3472, 3263, 3095, 1744, 1552, 1440, 1328, 1244, 1164, 832

can primarily be reduced to proving the following critical points: the lack of an epoxynorbornane fragment and the presence of a hydroxyl, not an N–H, group.

The second point was settled when analyzing the IR spectra of compound **7c** solutions in carbon tetrachloride, since the band at 3632 cm^{-1} was a sufficient proof in favor of the hydroxyl group. The potentialities of IR spectroscopy in the solution of the first problem turned out to be limited, since the absorption in the region 3040–3030 and 850–840 cm^{-1}, characteristic of epoxynorbornanes (νC–H, νC–O of the epoxy cycle) [13,14], may also be attributed to that of the aromatic system.

The structures of the epoxidation products have been determined upon examining ^{1}H NMR spectra (Table 4) in which there are no signals of the epoxy ring protons in the region $\delta \sim 3$, typical of the epoxides of this series and the strong-field doublet at δ = 0.6–0.8 of the proton of the methylene bridge H^{7a} located over the epoxy ring and effectively shielded by this fragment [15]. Two single-proton signals in the region δ = 3.4–3.7, i.e., the broadened singlet of the proton H^{2n} and the doublet of the proton H^{3x} split as a result of the spin–spin interaction with the prebridge proton H^7 with the substantial vicinal constant (up to 5.2 Hz), are characteristic of the spectra of the compounds obtained (Table 4). When cyclization does not occur, this constant does not usually exceed 3 or 4 Hz [9]. In the strong-field spectral region δ = 0.8–0.9, there is a signal of the H^{9n} proton split into a triplet of doublets due to interaction with the protons H^{9x}, H^6, and H^{8s} (Table 4). When recording the spectra, deuterochloroform and deuteroacetone were used as solvents, and both of these solvents were used for measuring the spectrum of compound **8b**. The signals in the weak-field region of the spectrum were easily assigned when deuterochloroform was used; however, in this case, the signals H^6 and H^{9x} are observed to superimpose on each other. On the contrary, the use of deuteroacetone makes the assignment of the signals for the weak-field protons H^2, H^3, and H^5 more complicated. In the ^{13}C NMR spectra of compounds (**8b**, **8h**), there are no signals for the epoxy ring carbons in the region δ = 49–51, typical of epoxynorbornanes [16].

Careful investigation of the structures of epoxidation products of the aromatic sulfonamides (**7a–j**) is of major significance in the context of recent results of the study of the reaction of *N*-(perfluorobutylsulfonyl) bicyclo[2.2.1]hept-2-en-endo-5-methylamine (**10**) with peroxyphthalic acid to yield the corresponding epoxide (**11**) [11].

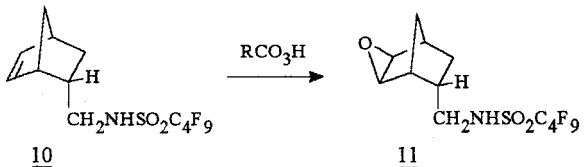

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TABLE 4 ^{1}H NMR Spectra of Compounds **8b**, **e**–**h**, **1** (δ/J Hz)

Compound	H^1	H^2	H^3	H^{5A}	H^{5B}	H^6	H^7	H^{8s}	H^{8a}	H^{9x}	H^{9n}
8b[a]	2.10	3.54	3.58 $^3J_{3,7}$4.8	3.17	(2H)	2.23	2.18	1.85 $^2J_{8s,8a}$9.5	1.33	1.82 $^2J_{9x,9n}$12.4 $^3J_{9x,6}$9.0 $^3J_{9x,1}$5.4	0.88 $^3J_{9n,6}$2.5 $^4J_{9n,8s}$2.5
8e[a]	2.16	3.52	3.62 $^3J_{3,7}$5.1	3.23 $^2J_{5A,5B}$8.9	3.15	2.28	2.21	1.87 $^2J_{8s,8a}$10.2	1.30	1.82 $^2J_{9x,9n}$12.5 $^3J_{9x,6}$9.9 $^3J_{9x,1}$5.0	0.82 $^3J_{9n,6}$2.3 $^4J_{9n,8s}$2.3
8e[b]	2.11	3.66	3.51 $^3J_{3,7}$5.2	3.23 $^2J_{5A,5B}$9.4 $^3J_{5,6}$4.4	3.04	2.10	2.18	1.85 $^2J_{8s,8a}$11.0	1.34	1.85 $^2J_{9x,9n}$12.8	0.92 $^3J_{9n,6}$2.2 $^4J_{9n,8s}$2.0
8f[b]	2.12	3.67	3.54 $^3J_{3,7}$5.0	3.25 $^2J_{5A,5B}$9.7 $^3J_{5,6}$4.8	3.06	2.23	2.16	1.87 $^2J_{8s,8a}$11.4	1.34	1.80 $^2J_{9x,9n}$12.5	0.91 $^3J_{9n,6}$2.6 $^4J_{9n,8s}$2.6
8g[a]	2.09	3.48	3.55 $^3J_{3,7}$5.2	3.13	(2H)	2.27	2.15	1.81 $^2J_{8s,8a}$10.0	1.27	1.78 $^2J_{9x,9n}$12.4 $^3J_{9x,6}$9.9 $^3J_{9x,1}$4.5	0.83 $^3J_{9n,6}$2.3 $^4J_{9n,8s}$2.3
8h[b]	2.14	3.66	3.55 $^3J_{3,7}$5.1	3.29 $^2J_{5A,5B}$9.3 $^3J_{5,6}$4.3	3.07	2.22	2.22	1.88 $^2J_{8s,8a}$10.1	1.36	1.86 $^2J_{9x,9n}$13.1	0.93 $^3J_{9n,6}$2.4 $^4J_{9n,8s}$2.3
8j[a]	2.10	3.53	3.58 $^3J_{3,7}$4.9	3.17	(2H)	2.21	2.16	1.88 $^2J_{8s,8a}$10.0	1.35	1.82 $^2J_{9x,9n}$12.6 $^3J_{9x,6}$9.2 $^3J_{9x,1}$5.0	0.89 $^3J_{9n,6}$2.5 $^4J_{9n,8s}$2.5

Solvent is [a]deuterochloroform and [b]deuteroacetone.

Apparently, the different behavior of the sulfonamides (**7a**–**j**) as against (**10**) is determined by the different nucleophilicities of the nitrogen atoms in these compounds. This is corroborated by the simplest analogs of sulfonamides whose *p*K*a* values are given below:

$PhSO_2NH_2$	$PhSO_2NHCH_3$	$CF_3SO_2NH_2$	$CF_3SO_2NHCH_3$
10.00	11.43	6.33	7.56

Substantial differences in *p*K*a* values can account for the completely different behavior of the aromatic and fluorinated sulfonamides. The electron density on the nitrogen in the series of sulfonamides (**7a**–**j**) turns out to be sufficient for stereochemically favorable attack and for intramolecular cyclization. Similar cases of cyclizations related to conformationally labile unsaturated tosylates have recently become well known [17].

STRUCTURAL DATA

The molecular structure of compound (**8j**) was determined by X-ray diffraction analysis. The coordinates of nonhydrogen atoms of compound (**8j**) are given in Table 5.

The perspective view of the molecule is shown in Figure 1. The average value for the length of the Csp^3–Csp^3 bond in the polycyclic skeleton of the molecule is 1.532 Å. The atom N(1) is of the tetrahedral configuration; its deviation from the plane SC(2)C(8) is 0.304 Å. An additional bond between the atoms C(2) and C(4) brings about countertwisting [18] of the norbornane system C(1)C(2)C(3)C(4)C(5) C(6)C(7). Figure 2 shows a projection of the molecular fragment along the direction C(3). . .C(6).

The double bond C(15) = O(4) is conjugated with the π-system of the aryl ring, with the torsion angles C(13)C(12)N(2)C(15) and C(12)N(2)C(15) O(4) being −4.1 and 0.9°, respectively. Due to such orientation of the keto group C(15) = O(4), a shortened intramolecular nonvalent contact between the atoms H(13) and O(4) is initiated. The distance H(13)–O(4) is 2.30 Å, whereas the length of the "normal" Van-der-Waals contact H. . .O is 2.45 Å. Steric repulsion of the atoms H(13) and O(4) results in an increase in the valence angles C(13)–C(12)–N(2), C(12)–N(2)–C(15), and N(2)–C(15)–O(4) to 124.8, 128.2, and 126.6°, respectively. Thus, relaxation of tension induced by the steric interaction between the

TABLE 5 Coordinates of Atoms and Their Equivalent Isotropic Temperature Factors B_{eq} (Å^2) in Structure **7j**

Atom	*x*	*y*	*z*	*B(Å^2)*
S	0.18412 (2)	0.44936 (9)	0.66975 (3)	4.04 (2)
O(1)	0.40254 (7)	0.33170 (3)	0.78630 (1)	4.74 (5)
O(2)	0.21506 (8)	0.36960 (3)	0.74423 (9)	5.37 (5)
O(3)	0.14703 (8)	0.60370 (3)	0.65430 (1)	5.51 (5)
O(4)	0.06219 (8)	−0.28600 (3)	0.44600 (1)	5.51 (5)
O(5)	−0.02972 (8)	−0.23770 (3)	0.33060 (1)	5.41 (5)
N(1)	0.23969 (8)	0.49690 (3)	0.65480 (1)	4.02 (5)
N(2)	0.01348 (9)	−0.02460 (3)	0.41290 (1)	4.27 (6)
C(1)	0.35850 (1)	0.45080 (4)	0.72800 (1)	3.99 (6)
C(2)	0.29090 (1)	0.37120 (3)	0.67300 (1)	3.71 (6)
C(3)	0.28640 (1)	0.34750 (4)	0.59640 (1)	5.18 (7)
C(4)	0.27050 (1)	0.53250 (4)	0.56630 (2)	5.57 (8)
C(5)	0.33630 (1)	0.62350 (5)	0.61630 (2)	6.34 (8)
C(6)	0.38100 (1)	0.48490 (5)	0.67300 (2)	5.35 (8)
C(7)	0.35620 (1)	0.32390 (5)	0.62140 (2)	6.58 (8)
C(8)	0.22100 (1)	0.59140 (5)	0.58320 (2)	5.76 (8)
C(9)	0.13209 (9)	0.30080 (3)	0.59850 (1)	3.80 (6)
C(10)	0.07680 (1)	0.35980 (4)	0.53170 (1)	4.24 (6)
C(11)	0.03860 (1)	0.24800 (4)	0.47220 (1)	4.35 (7)
C(12)	0.05460 (1)	0.07580 (3)	0.47760 (1)	3.62 (6)
C(13)	0.10880 (1)	0.01580 (3)	0.54520 (1)	3.97 (6)
C(14)	0.14800 (1)	0.12690 (4)	0.60540 (1)	3.95 (6)
C(15)	0.01970 (1)	−0.19160 (4)	0.40140 (1)	3.97 (6)
C(16)	−0.03390 (2)	−0.41590 (5)	0.31110 (2)	6.60 (1)
H(01)	0.38500 (1)	0.26600 (4)	0.80500 (1)	3.90 (7)
H(N2)	−0.01670 (9)	0.26600 (3)	0.37600 (1)	1.00 (5)

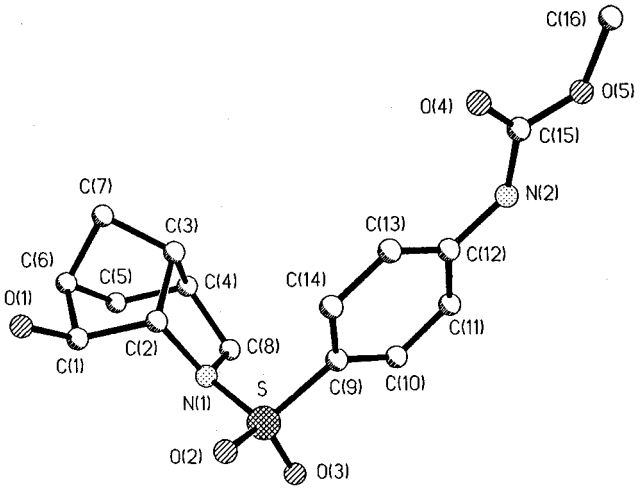

FIGURE 1 The perspective view of the molecule (**8j**).

atoms H(13) and O(4) occurs, not at the expense of disturbing the conjugation of the π-systems, but at the expense of increasing the valence angles at the atoms C(12), N(2), and C(15).

In the structure, there are hydrogen bonds of two types, i.e., O–H. . .O and N–H. . .O (Table 6). The

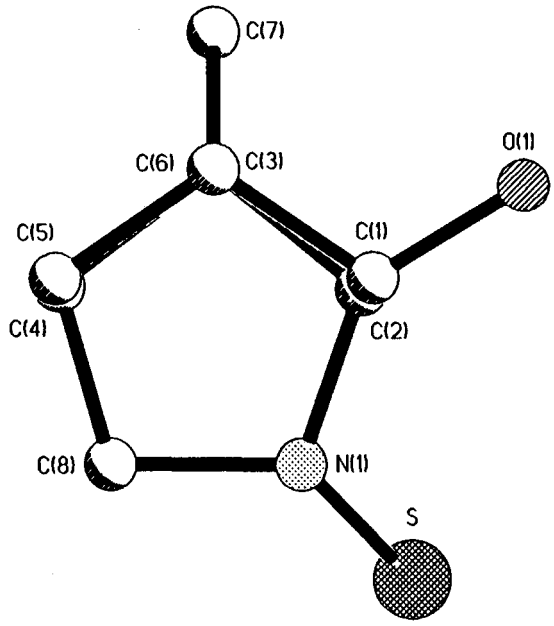

FIGURE 2 The projection of the molecule (**8j**) fragment along the diretion C(3). . .C(6).

TABLE 6 Hydrogen Bonds in Structure **8j**

		Distance (A)		*Angle (grade)*
Donor	*Acceptor*	*D...A*	*H...A*	*D-H...A*
O(1)	O(3) [0.5-*x*; 0.5-*y*; 1.5-*z*]	2.796	1.92	174
N(2)	O(1) [0.5-*x*; 0.5-*y*; 0.5-*z*]	2.957	2.14	175

molecules are united into spirals aligned along the *y*-axis by the hydrogen bonds O(1)–H(O1). . .O(3), whereas the latter N(2)–H(N2). . .O(1) combine the above spirals into layers oriented in parallel with the crystallographic plane (101).

EXPERIMENTAL

IR-spectra were recorded on Specord-80 M and Specord-75-IR instruments in the region 4000–400 cm^{-1} using KBr pellets. NMR spectra were measured on a Varian VXR 200 radiospectrometer (the operating frequency for the ^{1}H nuclei being 200 MHz; for the ^{13}C nuclei, 50.30 MHz) in deuterochloroform or deuteroacetone solutions using the domestic standard HMDS. TLC data were obtained using the Silufol UV-254 plates with ether as an eluent and iodine vapor as a developer. Elemental analyses were carried out on a Karlo Erba analyzer.

The syntheses of the unsaturated nitrile (**6**) and

the amine (**5**) were performed by methods described in the literature [8,9], and the yields were 96 and 74%, respectively.

N-(Arylsulfonyl)bicyclo[2.2.1]hept-2-en-endo-5-methylamines (**7a–j**). To a stirred emulsion (1.23 g, 0.01 mol) of amine (**5**) in ether (10 mL) and a 20% aqueous solution of sodium hydroxide (2 mL), a solution (0.01 mol) of the corresponding arylsulfonylchloride in ether (10 mL) was added dropwise. Termination of the reaction was determined by TLC monitoring. The organic layer was separated from the aqueous layer, and the solvent was removed by distillation. The product, with the impurities of the salt formed, was dissolved in the mixture chloroform–water (1:1)(20 mL). The organic layer was isolated, dried with the calcinated magnesium sulfate, and the solvent was removed. Physical properties and spectral characteristics of the compounds are provided in Tables 1 and 2.

N-(Arylsulfonyl)-exo-2-hydroxy-4-azatricyclo[4.2.1.0^{3,7}]nonanes (**8a–j**). *Method A.* The olefin (0.01 mol) and ethyl acetate (20 mL) were placed in a 100 mL flask, and 75–85% monoperoxyphthalic acid (0.02 mol) was gradually added under stirring. Termination of the reaction was determined by TLC monitoring. The phthalic acid that had formed was neutralized by addition of a saturated sodium carbonate solution until a pH of 7–8 was attained. The organic layer was collected, and the aqueous layer was extracted with chloroform three times. The united organic layer was dried with calcinated magnesium sulfate, the solvent was removed, and the product was purified.

Method B. The olefin (0.01 mol), urea (0.3 g, 0.005 mol), and 30% hydrogen peroxide (0.18 mL, 0.02 mol) in ethyl acetate (20 mL) were placed in a 100 mL flask. Powdered phthalic anhydride (0.29 g, 0.02 mol) was gradually added under stirring. Termination of the reaction was determined by TLC monitoring. The phthalic acid that had formed was neutralized by the addition of saturated sodium carbonate solution until a pH of 7–8 was attained. The organic layer was collected, and the aqueous layer was extracted with chloroform three times. The united organic layer was dried with calcinated magnesium sulfate, and the solvent was removed and the product purified. Physical and spectral characteristics of the compounds are given in Tables 3 and 4.

N-(perfluorobutylsulfonyl)bicyclo[2.2.1]hept-2-en-endo-5-methylamine (**10**) and *N*-(perfluorobutylsulfonyl)-exo-2,3-epoxy-bicyclo[2.2.1]heptane-endo-5-methylamine (**11**) were prepared according to methods described in the literature [11] in the yield 91 and 94%, respectively.

Crystal data for **8j**. $C_{16}H_{20}N_2O_5S$, M = 352.41, monoclinic, a = 24.732 (10), b = 7.803 (6), c = 20.622 (10) Å, β = 123.30 (4)°, V = 3326 (7) Å^3, Z = 8, d_c = 1.41 g·cm^{-3}, space group C2/C, μ = 19.4 cm^{-1}, F(000) = 1488.

All crystallographic measurements were made at 25°C using an Enraf Nonius CADY + diffractometer operating in the $\omega/2\Theta$ scan mode. The intensity data were collected within the range $1 \leq \Theta \leq 56^0$ using graphite monochromated Cu-K_α radiation (λ = 1.54184 Å). Intensities of 2353 unique reflections were measured. The structure was solved by the direct method and refined by full-matrix least-squares techniques in the anisotropic approximation. In the refinement, 1972 reflections with $I > 36(I)$ were used. Positions of all H atoms except at the O(1) and N(2) atoms, which were derived from the Fourier synthesis, were calculated and included in the final refinement with the fixed positional and thermal (B_{iso} = 5 Å^2) parameters. Convergence was obtained at R = 0.045 and R_w = 0.075, GOF = 2.94 (225 refined parameters; largest shift/esd after final cycle < 0.09; the largest peak in the final difference map, 0.56 e/Å^3). The weighting scheme $W = (G^2F + 0.0016F^2)^{-1}$ was used. Corrections for Lorentz and polarization effects but not for absorption were applied. All structural calculations were carried out with a PDP-11/23 + computer using the SDP-plus program package [19]. Full crystallographic data have been deposited at the Cambridge Crystallographic Data Centre.

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