References

Baert, F., Fouret, R., Oonk, H. A. J. & Kroon, J. (1978). *Acta Cryst.* B34, 222–226.

Bernal, I., Cai, J., Massoud, S. S., Watkins, S. F. & Fronczek, F. R. (1996). *J. Coord. Chem.* 38, 165–181.

Bigoli, F., Lanfranchi, M., Leporati, E., Nardelli, M. & Pellinghelli, M. A. (1981). *Acta Cryst.* B37, 1258–1265.

Flack, H. D. (1983). *Acta Cryst.* A39, 876–881.

Furberg, S. & Hassel, O. (1950). *Acta Chem. Scand.* pp. 1020–1023.

Furusaki, A., Abe, K. & Matsumoto, T. (1982). *Bull. Chem. Soc. Jpn,* 55, 611–612.

Jacques, J., Collet, A. & Wilen, S. H. (1981). *Enantiomers, Racemates, and Resolutions,* p. 81. New York: John Wiley.

Martin, S. F. & Barr, K. J. (1996). *J. Am. Chem. Soc.* 118, 3299–3300.

Martin, S. F. & Bur, S. K. (1997). *Tetrahedron Lett.* 44, 7641–7644.

Mostad, A., Romming, C. & Tressum, L. (1975). *Acta Chem. Scand. Ser. B,* 29, 171–176.

Schouwstra, Y. (1973). *Acta Cryst.* B29, 1636–1641.

Sheldrick, G. M. (1994). *SHELXTL-Plus.* Release 5.03. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Siemens (1994). *XSCANS User's Manual.* Version 2.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

N,N-Bis(p-nitrophenylsulfonyl)cyclohexyl-amine

Joseph S. Brunzelle,[a] Veronica A. Curtis-Palmer[b] and Stephen F. Pavkovic[a]

[a]*Department of Chemistry, Loyola University Chicago, Chicago, IL 60626, USA, and* [b]*Department of Chemistry, Northeastern Illinois University, Chicago, IL 60625, USA. E-mail: spavko1@luc.edu*

Abstract

The title compound ($C_{18}H_{19}N_3O_8S_2$) undergoes pyrolytic reaction to yield cyclohexene and N,N,-bis(p-nitrophenylsulfonyl)amine without rearrangement. Non-bonded contacts between oxygen and β-carbon H atoms were thought to be important in the reaction mechanism, but distances were found to be very similar to those present in a derivative which does not undergo pyrolysis.

Comment

N,N-Disulfonimide derivatives of certain alkyl amines stereoselectively pyrolyze to form alkenes in high yields and without skeletal rearrangement (Curtis *et al.*, 1981). The reaction only occurs when the α-C atom on the parent amine is tertiary. A mechanism was proposed that involved a β-H atom linked to an

O atom in the transition state. This suggested that preferred orientations at α- and/or β-C atoms might determine whether or not a given compound underwent pyrolysis. Accordingly, structure determinations were planned for the N-alkyl-N,N-disulfonimide compounds tested. We have reported the structure of the non-reactive compound N,N-bis(p-nitrophenylsulfonyl)-phenethylamine (Curtis & Pavkovic, 1983). Now we wish to report the structure of the reactive cyclohexylamine derivative, (I), which forms cyclohexene upon pyrolysis.

(I)
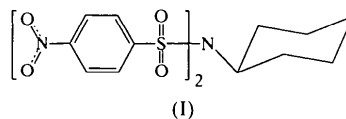
Selected bond distances and angles are listed in Table 1. Fig. 1 shows a diagram of the molecule. The central feature in this structure is the nearly planar grouping of the amine-N atom and the three atoms bonded to it. The N is bonded to two S and a tertiary C atom from the cyclohexyl group. The N atom is 0.10 (4) Å out of the plane defined by its bonded atoms.
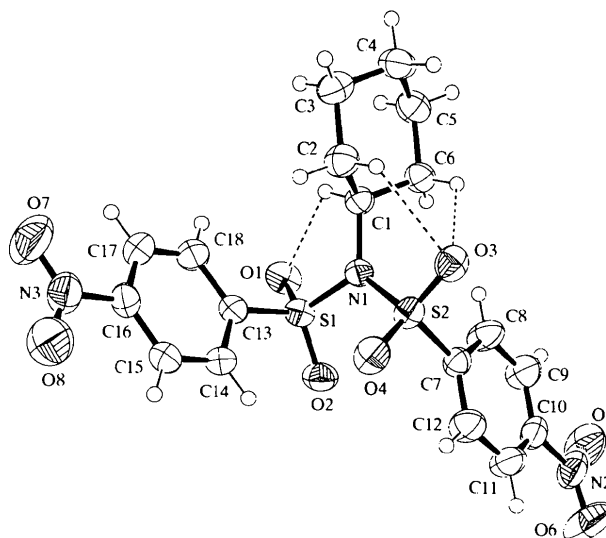

Fig. 1. An *ORTEP*III molecular structure diagram showing non-H atoms at 50% probability. Short non-bonded contacts between O and α- and β-C H atoms are shown as dashed lines.

Bond distances from each S to like target atoms are the same in both cases and comparable angles about S are very similar. However, orientations about S—N bonds for S-bonded p-nitrophenyl groups are decidedly different as shown by torsion angles of $-82.9\,(1)°$ for C1—N1—S1—C13 and $-117.8\,(1)°$ for C1—N1—S2—C7. Least-squares planes of the two phenyl rings

are approximately parallel to each other [12.4 (1)°], and both are nearly normal to the plane of the four central atoms C1, N1, S1 and S2 [79.1 (1) and 87.6 (1)° for rings bonded to S1 and S2, respectively].

The cyclohexyl ring has a chair conformation. The least-squares plane of atoms in the 'seat' of the chair (C2, C3, C5, and C6) is approximately normal to the plane of four central atoms [86.6 (1)°] and is nearly parallel to the phenyl rings [16.9 (1) and 6.3 (2)°, respectively, as above]. The shortest non-bonded H—O contact distances involve H atoms on the α- and β-C atoms. H1 on C1(α) is 2.316 (2) Å from O1, and H2*A* and H6*B* on C2(β) and C6(β) are 2.454 (2) and 2.481 (2) Å, respectively, from O3.

Comparison with the structure of the previously reported non-reactive 2-phenethyl compound shows that it has similar short intramolecular H—O contact distances of 2.243 (2) and 2.379 (2) Å for α and β atoms, respectively. In summary, almost all bonding parameters for the two compounds are quite similar, so structural differences do not provide an answer for their opposite behavior upon pyrolysis. The only differentiating feature of note is the C—N—S—O torsion angle for the O atom making the closest contact to the β-H atom. For the active compound, the C1—N1—S2—O3 torsion angle is −4.4 (2)° whereas for the non-reactive compound the comparable angle is 45.6 (2)°. Additional examples would be needed to show whether or not this is a critical feature.

Structures for several alkyl-substituted disulfonimide compounds have been reported, but the criterion used for their consideration here was the orientation of the two SO_2 groups relative to the N—C bond. The S—O vectors in the two groups are related by a pseudo twofold rotation about the N—C bond. Reported compounds with similar SO_2 group orientations include *N*-methyldimesylamine (Blaschette *et al.*, 1991), *N*-methylbis(4-methylbenzosulfonyl)amine (Jones *et al.*, 1995), *N*-(cyclopropylmethyl)dimesylamine (*ibid.*), and *N*-(benzyl)dimesylamine (Henschel *et al.*, 1997). Tabulation of bond parameters for these compounds showed only minor variations among bond distances involving the amine N, and also among bond angles with amine N at the vertex. All compounds contain α-H atom(s) with contact distances to O atoms ranging from 2.342 (4) to 2.672 (4) Å, comparable to similar distances found in our compounds. Only *N*-(cyclopropylmethyl)dimesylamine contains a β-H atom and its closest O atom contact is 2.826 (4) Å, which is significantly longer than those found in our compounds. The largest variance occurs among C—N—S—C torsion angles, as was noted for the title compound. All told, these compounds, although similar to ours, offer little insight for better understanding of the pyrolysis reaction. Perhaps the reaction depends on development of carbocation character in the transition state as opposed to preferred orientations for α- and β-H atoms.

Experimental

The title compound was prepared by reaction of cyclohexylamine with *p*-nitrobenzenesulfonyl chloride in *N,N*-dimethylformamide (15%)/H_2O at 353 K and pH 8–9, to form the sulfonamide. Treatment of the latter with NaH and a second equivalent of *p*-nitrobenzenesulfonyl chloride in dry *N,N*-dimethylformamide gave the final product. Crystals suitable for diffraction were obtained by evaporation of acetone solutions.

Crystal data

$C_{18}H_{19}N_3O_8S_2$	Mo $K\alpha$ radiation
$M_r = 469.48$	$\lambda = 0.71070$ Å
Monoclinic	Cell parameters from 18
$P2_1/a$	reflections
$a = 15.640 (4)$ Å	$\theta = 10–15°$
$b = 22.765 (6)$ Å	$\mu = 0.317$ mm^{-1}
$c = 5.681 (1)$ Å	$T = 295 (2)$ K
$\beta = 92.663 (5)°$	Prism
$V = 2020.5 (8)$ Å^3	$0.60 \times 0.45 \times 0.36$ mm
$Z = 4$	Colourless
$D_x = 1.543$ Mg m^{-3}	
$D_m = 1.54 (2)$ Mg m^{-3}	
D_m measured by flotation in mixed organic liquids	

Data collection

Picker FACS–I diffractometer	3238 reflections with $I > 2\sigma(I)$
ω–2θ scans	$R_{int} = 0.030$
Absorption correction:	$\theta_{max} = 27.50°$
ψ scan (Pavkovic *et al.*, 1978)	$h = -20 \rightarrow 20$
	$k = -27 \rightarrow 29$
$T_{min} = 0.86$, $T_{max} = 0.89$	$l = -7 \rightarrow 2$
10 425 measured reflections	5 standard reflections
4653 independent reflections	every 200 reflections
	intensity decay: none

Refinement

Refinement on F^2	$\Delta\rho_{max} = 0.255$ e Å^{-3}
$R[F^2 > 2\sigma(F^2)] = 0.039$	$\Delta\rho_{min} = -0.263$ e Å^{-3}
$wR(F^2) = 0.104$	Extinction correction:
$S = 1.004$	*SHELXL93* (Sheldrick,
4653 reflections	1993)
281 parameters	Extinction coefficient:
H atoms not refined	0.0172 (13)
$w = 1/[\sigma^2(F_o^2) + (0.0417P)^2]$	Scattering factors from
where $P = (F_o^2 + 2F_c^2)/3$	*International Tables for*
$(\Delta/\sigma)_{max} = 0.001$	*Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

S1—O1	1.4211 (14)	S2—N1	1.671 (2)
S1—O2	1.4221 (14)	N1—C1	1.520 (2)
S1—N1	1.674 (2)	C1—C2	1.516 (3)
S2—O4	1.4191 (14)	C1—C6	1.520 (3)
S2—O3	1.4220 (14)		
O1—S1—O2	121.45 (9)	O4—S2—C7	107.81 (9)
O1—S1—N1	105.91 (8)	O3—S2—C7	107.31 (9)
O2—S1—N1	106.58 (8)	N1—S2—C7	105.61 (8)
O1—S1—C13	107.83 (9)	C1—N1—S2	122.65 (12)
O2—S1—C13	108.37 (9)	C1—N1—S1	118.07 (12)
N1—S1—C13	105.65 (8)	S2—N1—S1	118.22 (9)

O4—S2—O3	119.76 (9)	C2—C1—N1	113.99 (15)
O4—S2—N1	109.97 (8)	C2—C1—C6	112.6 (2)
O3—S2—N1	105.52 (8)	N1—C1—C6	112.55 (15)

Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ORTEP*III (Burnett & Johnson, 1996).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: DA1049). Services for accessing these data are described at the back of the journal.

References

Blaschette, A., Naveke, M. & Jones, P. G. (1991). *Z. Naturforsch. Teil B*, **46**, 5–14.
Burnett, M. N. & Johnson, C. K. (1996). *ORTEP*III. *Oak Ridge Thermal Ellipsoid Plot Program for Crystal Structure Illustrations*. Report ORNL-6895. Oak Ridge National Laboratory, Tennessee, USA.
Curtis, V. A., Knutson, F. J. & Baumgarten, R. J. (1981). *Tetrahedron Lett.* **22**, 199–202.
Curtis, V. A. & Pavkovic, S. F. (1983). *Acta Cryst.* C**39**, 1077–1078.
Henschel, D., Blaschette, A. & Jones, P. G. (1997). *Acta Cryst.* C**53**, 1669–1671.
Jones, P. G., Hamann, T., Schaper, W., Lange, I. & Blaschette, A. (1995). *Phosphorus Sulfur Silicon*, **106**, 91–104.
Pavkovic, S. F., Wilhelm, F. C. & Brown, J. N. (1978). *Acta Cryst.* B**34**, 1337–1340.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.

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ap-9-(o-tert-Butylphenyl)-9-methylthio-fluorene, the first isolated ap rotamer of a 9-substituted 9-(o-tert-butylphenyl)fluorene

Cal Y. Meyers,[a] Yuqing Hou[a] and Paul D. Robinson[b]

[a]*Department of Chemistry and Biochemistry, Southern Illinois University-4409, Carbondale, IL 62901, USA, and* [b]*Department of Geology, Southern Illinois University-4324, Carbondale, IL 62901, USA. E-mail: robinson@geo.siu.edu*

Abstract

Treatment of sp-9-(o-tert-butylphenyl)-9-fluorenol with HBr and methanethiol provided ap-9-(o-tert-butyl-phenyl)-9-methylthiofluorene, $C_{24}H_{24}S$, exclusively, the first isolated ap rotamer of a 9-substituted 9-(o-tert-butylphenyl)fluorene. The ap configuration in this series, generally the thermodynamically less favored, is preferred in the case of the title compound because the even larger interaction between the tert-butyl group and

S in the sp configuration is energetically forbidden. The extensive distortion in the title compound is obvious from its X-ray structure and the associated geometric parameters.

Comment

As part of our recent studies of rotationally restricted 9-substituted fluorenes (Hou, 1997), we prepared 9-(o-tert-butylphenyl)-9-methylthiofluorene, (2). We found that, while 9-(o-tert-butylphenyl)-9-fluorenol, (1), 9-(o-tert-butylphenyl)-9-methoxyfluorene, (3), and 9-(o-tert-butylphenyl)-9-ethoxyfluorene, (4), exist solely in their sp configurations, (2) exists exclusively in its ap configuration, both in solution and in its crystalline state (Meyers et al., 1997; Robinson et al., 1998). The strong steric repulsion between the tert-butyl group and the fluorene π cloud makes the ap configuration highly unstable (Nakamura et al., 1977; Ōki, 1993; Meyers et al., 1995, 1997). Our finding that the ap configuration of (2) is the exclusive form tells us that the 9-methylthio group enforces the ap configuration which, although highly energetic per se, is nonetheless thermodynamically favored over the sp configuration in this case. Compound (2) is the first isolated ap rotamer of a 9-substituted 9-(o-tert-butylphenyl)fluorene.
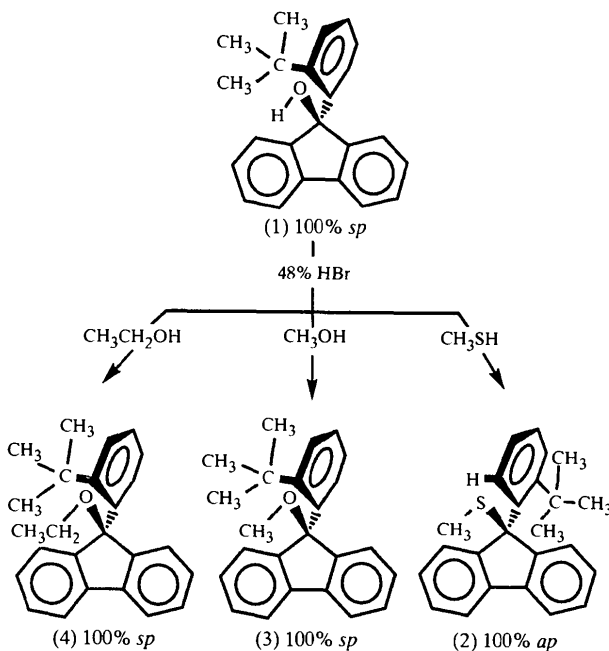
The extensive distortions in ap (2) are displayed in its X-ray structure, which is shown in Fig. 1 with the atom-numbering scheme. The selected geometric parameters compared in Table 1 clearly illustrate the strain in (2). This strain accounts for its unusual instability, which leads to its facile homolytic decomposition at room temperature, in contrast to the thermal stability