Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

Dicyclohexylammonium 4-nitrophenylsulfinate

Iván Brito,[a]* Matías López-Rodríguez,[b] Alejandro Cárdenas[c] and Andrea Reyes[a]

[a]Departamento de Química, Facultad de Ciencias Básicas, Universidad de Antofagasta, Casilla 170, Antofagasta, Chile, [b]Instituto de Bio-Orgánica 'Antonio González', Universidad de La Laguna, Astrofísico Francisco Sánchez N°2, La Laguna, Tenerife, Spain, and [c]Departamento de Física, Facultad de Ciencias Básicas, Universidad de Antofagasta, Casilla 170, Antofagasta, Chile

Correspondence e-mail: ivanbritob@yahoo.com

Key indicators

Single-crystal X-ray study
T = 298 K
Mean σ(C–C) = 0.007 Å
Disorder in main residue
R factor = 0.082
wR factor = 0.243
Data-to-parameter ratio = 19.2

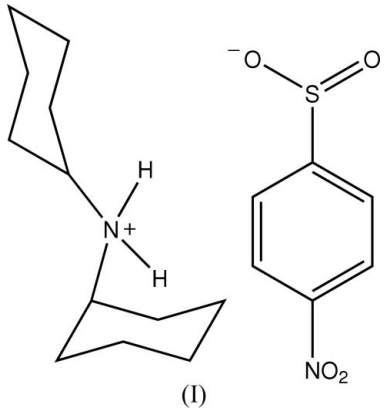
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Received 10 August 2006
Accepted 16 August 2006

In the crystal structure of the title compound, $C_{12}H_{24}N^{+}\cdot NO_2-C_6H_4-SO_2^{-}$, dimers are formed by N—H···O and C—H···O hydrogen-bond interactions. These dimers are located around centres of inversion.

Comment

The title compound, (I), was not the intended product of a reaction to make a sulfenamide. A search of the Cambridge Structural Data Base (CSD, Version 5.27; Allen, 2002) for the 4-nitrophenylsulfinate anion revealed that the title compound is the first crystal structure of a complex salt of this fragment. A view of the molecular structure of (I) is given in Fig. 1 and selected geometric parameters are listed in Table 1.



(I)

In the complex cation, one of the cyclohexyl rings (atoms C13–C18) has a chair conformation [puckering amplitude Q_T = 0.570 (6) Å, θ = 0.0 (6)° and φ = 128 (9)°], while in the other cyclohexyl ring (C7–C12), atoms C10 and C11 are disordered over two sites so that the ring adopts a distorted chair conformation, as seen from the puckering parameters [Q_T = 0.589 (9) Å, θ = 164.7 (10)° and φ = 129 (4)°] for the major disordered component. The minor disordered component has puckering parameters Q_T = 0.535 (8) Å, θ = 163.7 (10)° and φ = 260 (3)° (Cremer & Pople, 1975). The molecular dimensions in the complex cation of (I) (Table 1) are within normal ranges (Allen *et al.*, 1987), with the following mean bond distances: C—C = 1.521 (4) Å and C—N = 1.507 (4) Å. At the pyramidal S atom, the bond angles involving sulfinate atoms O1 and O2 are significantly larger than the C—S—O angle. The conformation of the SO_2 fragment, with the sulfinate atom O1 almost coplanar with the aryl ring, may be controlled by an intramolecular dipolar interaction involving positively charged atom H3 and negatively charged atom O1. The nitro group is essentially coplanar with the aryl group; a similar conforma-

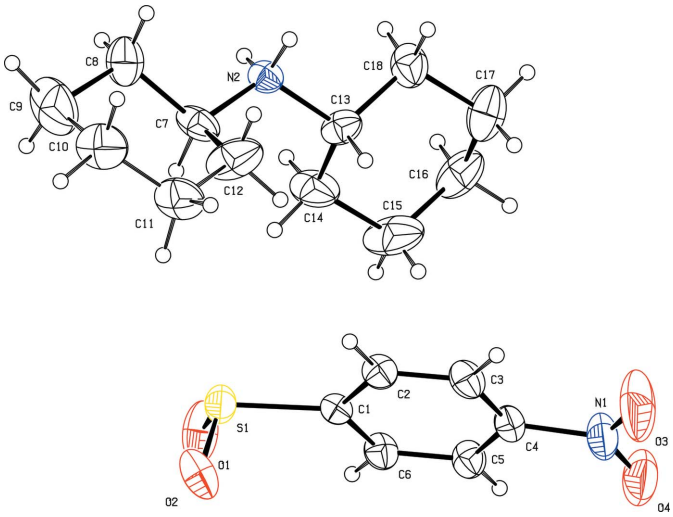


Figure 1
The molecular structure of (I), with displacement ellipsoids drawn at the 30% probability level. The disordered atoms C10′ and C11′ are not shown.

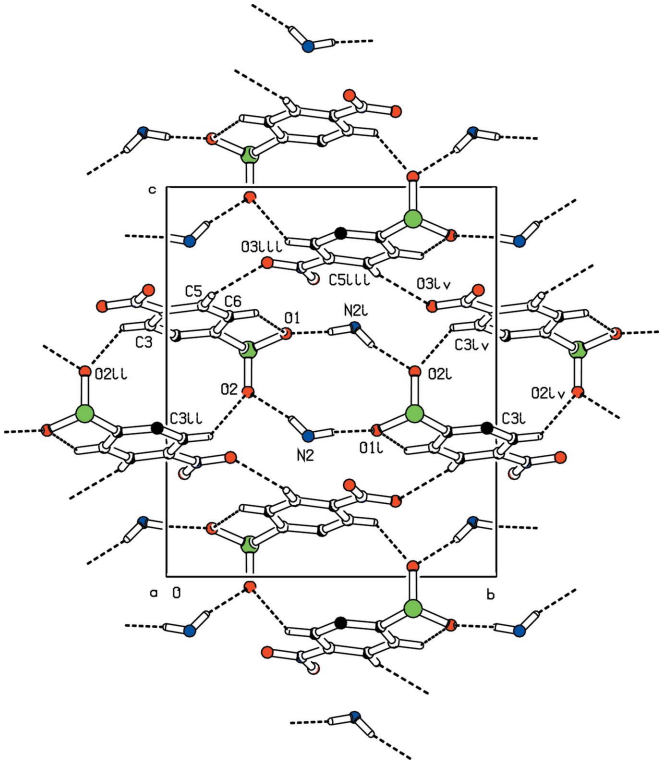


Figure 2
A view of part of the crystal structure of (I), showing the hydrogen-bond interactions. For the sake of clarity, H and cyclohexyl ring atoms not involved in the motif shown have been omitted. Hydrogen bonds are indicated by dashed lines. [Symmetry codes: (i) $-x+1, -y+1, -z+1$; (ii) $-x+1, -y, -z+1$; (iii) $-x+2, y+\frac{1}{2}, -z+\frac{3}{2}$; (iv) $x, y+1, z$.]

tion was found in the compound methyl 2-nitrophenyl sulfoxide (Ianelli *et al.*, 1992) as one representative example.

The crystal structure of (I) is built by an intramolecular C—H···O hydrogen bond and four intermolecular C—H···O and N—H···O hydrogen bonds. The intramolecular C6—H6···O1 interaction forms a five-membered ring, O1/S1/C1/C6/H6 (Fig. 2). Ring atom C3, which is adjacent to the nitro group and hence has the most polarized C—H bond in the molecule, acts as a hydrogen-bond donor to sulfinate atom O2 in the molecule at $(-x+1, -y, -z+1)$, forming an $R_2^2(12)$ dimer centred at $(\frac{1}{2}, 0, \frac{1}{2})$. Cation atom N2 acts as hydrogen-bond donor to sulfinate atom O2, which exhibits a bifurcated hydrogen bond, forming an $R_4^4(12)$ dimer centred at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ (Table 2 and Fig. 2) (Bernstein *et al.*, 1995).

Experimental

All reactions were carried out under an atmosphere of purified nitrogen. Solvents were dried and distilled prior to use. Bis(4-nitrophenyl) disulfide was purchased from Aldrich. The title compound was obtained as yellow block-shaped crystals in an attempt to prepare a sulfenamide by a known metal-assisted technique (Davis *et al.*, 1977). Into a 1000 ml three-necked flask equipped with an overhead stirrer was placed silver nitrate (7.8 g, 0.045 mol) in methanol (400 ml). After dissolution had taken place, an equivalent amount of bis(4-nitrophenyl) disulfide was added and the reaction mixture was cooled in an ice bath. An excess of dicyclohexylamine (5 equivalents) was added and the reaction mixture stirred overnight. The silver mercaptide which formed was filtered off and the solvent removed at reduced pressure and a temperature of 308–313 K. The resulting residue was dissolved in diethyl ether, washed with water (4 × 100 ml) and dried over $MgSO_4$. The compound was crystallized from methanol–water, collected by filtration and dried in a vacuum desiccator over $CaCl_2$. Yellow block-shaped crystals of (I) suitable for X-ray analysis were grown from a methanol–water solution (1:1 *v*/*v*) at 298 K over a period of a few days.

Crystal data

$C_{12}H_{24}N^+\cdot C_6H_4NO_4S^-$
$M_r = 368.48$
Monoclinic, $P2_1/c$
$a = 13.185\ (7)$ Å
$b = 11.407\ (5)$ Å
$c = 16.055\ (9)$ Å
$\beta = 122.906\ (5)^\circ$
$V = 2027.3\ (18)$ Å^3
$Z = 4$
$D_x = 1.207$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 0.18$ mm^{-1}
$T = 298\ (2)$ K
Block, yellow
0.45 × 0.25 × 0.19 mm

Data collection

Nonius KappaCCD area-detector diffractometer
φ scans, and ω scans with κ offsets
Absorption correction: multi-scan (*SORTAV*; Blessing, 1995)
$T_{min} = 0.950$, $T_{max} = 0.964$
5011 measured reflections
4389 independent reflections
3556 reflections with $I > 2\sigma(I)$
$\theta_{max} = 27.0^\circ$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.082$
$wR(F^2) = 0.243$
$S = 1.11$
4389 reflections
229 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.1198P)^2 + 1.1689P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.025$
$\Delta\rho_{max} = 0.45$ e Å^{-3}
$\Delta\rho_{min} = -0.42$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

S1—O2	1.480 (3)	O4—N1	1.202 (5)
S1—O1	1.496 (3)	N2—C7	1.502 (4)
S1—C1	1.817 (3)	N2—C13	1.512 (4)
O3—N1	1.206 (5)		
O2—S1—O1	108.7 (2)	O1—S1—C1	101.45 (15)
O2—S1—C1	101.23 (15)	C7—N2—C13	118.3 (3)
O1—S1—C1—C6	−13.9 (3)		

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N2—H100···O1^{i}	0.87 (4)	1.86 (4)	2.719 (5)	165 (4)
N2—H200···O2^{ii}	0.85 (4)	1.99 (4)	2.821 (5)	166 (4)
C3—H3···O2^{iii}	0.93	2.59	3.274 (5)	131
C5—H5···O3^{iv}	0.93	2.48	3.265 (7)	143
C6—H6···O1	0.93	2.49	2.874 (6)	105

Symmetry codes: (i) $-x+1, y-\frac{1}{2}, -z+\frac{3}{2}$; (ii) $x, -y+\frac{3}{2}, z-\frac{1}{2}$; (iii) $-x+1, -y+1, -z+2$; (iv) $-x, y+\frac{1}{2}, -z+\frac{3}{2}$.

Atoms C10 and C11 are severely disordered. They were modelled using a split model with refined population parameters [C10/C10′ = 0.535 (13)/0.465 (13); C11/C11′ = 0.535 (13)/0.465 (13)]. H atoms bonded to N2 were found in difference maps and were freely refined, while those bonded to carbon were positioned geometrically (C—H = 0.93–0.97 Å) and were refined with a riding model, with U_{iso}(H) = 1.2U_{eq}(C). The material was difficult to obtain in a suitable crystalline form and the best available specimen was lost late in the data collection.

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *DENZO-SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO-SMN*; program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997) and *PLATON* (Spek, 2003); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

This work was supported by grants from Fondecyt (No. 1030052) and Universidad de Antofagasta (No. DI-1324–06). We thank the Spanish Research Council (CSIC) for providing us with a free-of-charge license for the CSD.

References

Allen, F. H. (2002). *Acta Cryst.* B**58**, 380–388.
Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans. 2*, pp. S1–19.
Altomare, A., Burla, M. C., Camalli, M., Cascarano, G. L., Giacovazzo, C., Guagliardi, A., Moliterni, A. G. G., Polidori, G. & Spagna, R. (1999). *J. Appl. Cryst.* **32**, 115–119.
Bernstein, J., Davies, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
Blessing, R. H. (1995). *Acta Cryst.* A**51**, 33–38.
Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.
Davis, F. A., Friedman, A. J., Kluger, E. W., Skibo, E. B., Fretz, E. R., Milicia, A. P. & LeMasters, W. C. (1977). *J. Org. Chem.* **42**, 967–972.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
Ianelli, S., Musatti, A., Nardelli, M., Benassi, R., Folli, U. & Taddei, F. (1992). *J. Chem. Soc. Perkin Trans. 2*, pp. 49–57.
Nonius (1998). *KappaCCD Server Software*. Nonius BV, Delft, The Netherlands.
Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.
Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.
Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.