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Dicyclohexylammonium Bis(dimethyldithiocarbamyl)acetate

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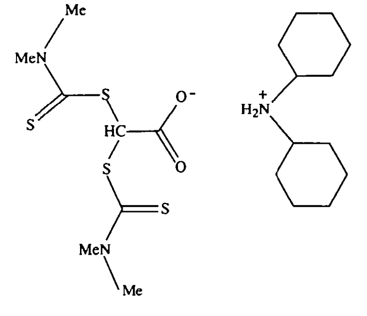
Abstract

The unit cell of dicyclohexylammonium bis(dimethyldithiocarbamyl)acetate, $C_{12}H_{24}N^+.C_8H_{13}N_2O_2S_4^-$, contains two independent ion pairs. The ammonium N atom is hydrogen bonded to the carboxylate O atom and also to the carboxylate O atom of the centrosymmetrically related anion to give rise to a O—C—O···N···O—C—O···N ring.

Comment

Dithiocarbamyl-substituted acetic acids possess plant growth-regulating properties (Fawcett, Wain & Wrightman, 1956; van der Kerk, van Raalte, Kaars Sijpesteijn & van der Veen, 1955) comparable with that of 3-indolylacetic acid and its derivatives (Domiano & Branca, 1990) despite the absence of an aromatic ring in their molecular structures, an apparently essential requirement for auxin activity. In the crystal structure of the hydrated dicyclohexylammonium salt of dimethyldithiocarbamylacetic acid, the ammonium cation [N···O = 2.738 (6) and 2.741 (6) Å] and the water molecule are hydrogen bonded to the carboxyl O atoms of adjacent carboxylato anions (Ng, 1992) to give rise to a three-dimensional network structure; both carboxyl O atoms are three-coordinate. The second electron-withdrawing dimethyldithiocarbamyl group in dicyclohexylammonium bis(dimethyldithiocarbamyl)-acetate decreases significantly the Lewis basicity of the carboxyl O atoms. The propensity for hydrogen bonding with the counterion is decreased; the atoms are only two-coordinate, being linked to only one ammonium cation. In molecule *A*, the ammonium cation is hydrogen bonded to one carboxylate O atom, and to the other carboxylate O atom belonging to the symmetry-related (1 − *x*, 1 − *y*, 2 − *z*) molecule; molecule *B* is similarly linked into a dimeric unit [*A*: N···O = 2.701 (3), 2.796 (3) Å; *B*: N···O = 2.698 (3), 2.837 (3) Å].



Other than a shorter C15—S1 bond in *A*, the ion pairs show no important differences in distances and angles. Bond dimensions of the cation and anion are similar

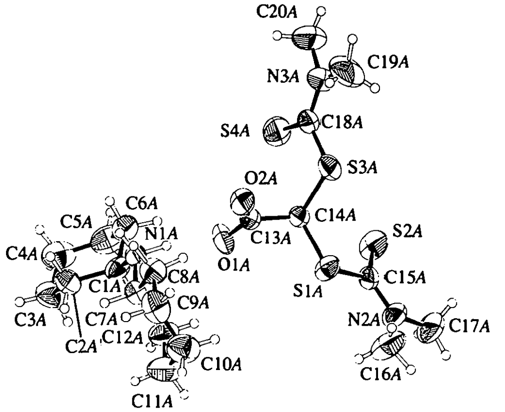


Fig. 1. *ZORTEP* (Zsolnai & Pritzkow, 1994) plot of *A* at the 50% probability level.

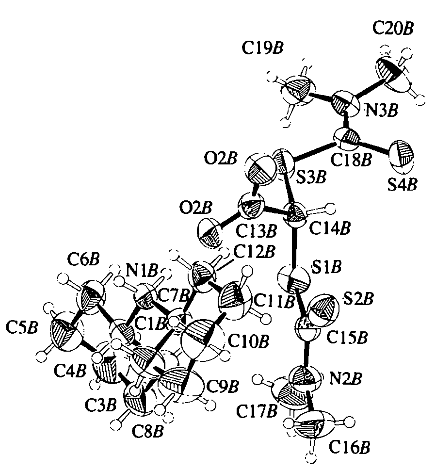


Fig. 2. *ZORTEP* (Zsolnai & Pritzkow, 1994) plot of *B* at the 50% probability level.

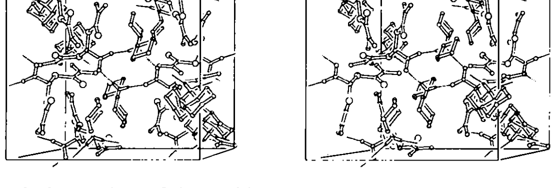


Fig. 3. Stereoview of the packing.

to the analogous values found in the dimethyldithiocarbamylacetate and also in dicyclohexylammonium *O*-(dimethylmonothiocarbamyl)acetate, which is also a centrosymmetric hydrogen-bonded [N···O = 2.706 (4), 2.750 (3) Å] dimeric compound (Ng, 1993).

Experimental

Bis(dimethyldithiocarbamyl)acetic acid was synthesized from sodium dimethyldithiocarbamate and dichloroacetic acid (Pluijgers & van der Kerk, 1959) and was recrystallized from ethanol. Equimolar amounts of the acid and dicyclohexylamine were then dissolved in a small volume of hot ethanol; slow cooling of the filtered solution gave crystals of the compound.

Crystal data

$C_{12}H_{24}N^+.C_8H_{13}N_2O_2S_4^-$
$M_r = 479.77$
Monoclinic
$P2_1/c$
$a = 17.649\,(3)$ Å
$b = 16.428\,(1)$ Å
$c = 18.743\,(3)$ Å
$\beta = 106.636\,(7)^\circ$
$V = 5207\,(1)$ Å^3
$Z = 8$
$D_x = 1.224$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 12–13^\circ$
$\mu = 0.385$ mm^{-1}
$T = 298$ K
Irregular
0.55 × 0.55 × 0.55 mm
Transparent

Data collection

Enraf–Nonius CAD-4 diffractometer
ω scans
Absorption correction: none
9450 measured reflections
9144 independent reflections
6384 observed reflections [$I > 2\sigma(I)$]

$R_{\rm int} = 0.0158$
$\theta_{\rm max} = 24.98^\circ$
$h = -20 \rightarrow 20$
$k = 0 \rightarrow 19$
$l = 0 \rightarrow 22$
3 standard reflections
frequency: 60 min
intensity decay: 5.2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0462$
$wR(F^2) = 0.1055$
$S = 1.059$
9144 reflections
539 parameters
U(H) = 1.5$U_{\rm eq}$(C); H atoms of the ammonium cations were located and refined
$w = 1/[\sigma^2(F_o^2) + (0.0586P)^2 + 1.7604P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\rm max} = 0.001$
$\Delta\rho_{\rm max} = 0.358$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.235$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
S1*A*	0.19521 (4)	0.46398 (5)	0.81933 (4)	0.0566 (2)
S2*A*	0.36404 (5)	0.41272 (7)	0.89036 (5)	0.0752 (3)
S3*A*	0.17551 (5)	0.31050 (4)	0.88993 (4)	0.0548 (2)
S4*A*	0.24900 (6)	0.32813 (6)	1.05415 (5)	0.0751 (3)
O1*A*	0.1464 (1)	0.5228 (1)	0.9683 (1)	0.0682 (6)
O2*A*	0.0582 (1)	0.4316 (1)	0.9088 (1)	0.0608 (6)
N1*A*	0.0508 (1)	0.6217 (2)	1.0187 (1)	0.0456 (6)
N2*A*	0.310 (1)	0.4830 (2)	0.7588 (1)	0.0591 (7)
N3*A*	0.1841 (2)	0.1935 (2)	0.9855 (2)	0.0801 (9)
C1*A*	0.1095 (2)	0.6699 (2)	1.0770 (2)	0.0511 (7)
C2*A*	0.0699 (2)	0.7344 (2)	1.1113 (2)	0.0632 (8)
C3*A*	0.1323 (2)	0.7812 (2)	1.1703 (2)	0.082 (1)
C4*A*	0.1823 (3)	0.7254 (2)	1.2295 (2)	0.086 (1)
C5*A*	0.2191 (2)	0.6582 (3)	1.1955 (2)	0.083 (1)
C6*A*	0.1580 (2)	0.6119 (2)	1.1354 (2)	0.0638 (8)
C7*A*	0.0022 (2)	0.6664 (2)	0.9515 (2)	0.0505 (7)
C8*A*	−0.0550 (2)	0.6062 (2)	0.9024 (2)	0.0588 (8)
C9*A*	−0.1042 (2)	0.6466 (2)	0.8317 (2)	0.079 (1)
C10*A*	−0.0531 (3)	0.6883 (2)	0.7901 (2)	0.086 (1)
C11*A*	0.0035 (3)	0.7474 (2)	0.8401 (2)	0.093 (1)
C12*A*	0.0540 (2)	0.7062 (2)	0.9099 (2)	0.0695 (9)
C13*A*	0.1252 (2)	0.4608 (2)	0.9297 (2)	0.0444 (6)
C14*A*	0.1919 (2)	0.4179 (2)	0.9053 (1)	0.0410 (6)
C15*A*	0.2964 (2)	0.4535 (2)	0.8203 (2)	0.0464 (7)
C16*A*	0.3892 (2)	0.4782 (3)	0.7494 (2)	0.089 (1)
C17*A*	0.2506 (2)	0.5228 (3)	0.6991 (2)	0.094 (1)
C18*A*	0.2030 (2)	0.2723 (2)	0.9818 (2)	0.0538 (7)
C19*A*	0.1388 (3)	0.1468 (2)	0.9208 (3)	0.112 (2)
C20*A*	0.2081 (3)	0.1499 (3)	1.0564 (3)	0.124 (2)
S1*B*	0.72751 (4)	0.21930 (5)	1.03054 (5)	0.0576 (2)
S2*B*	0.63051 (5)	0.19359 (6)	0.87249 (5)	0.0674 (2)
S3*B*	0.80033 (4)	0.07547 (5)	1.10254 (4)	0.0543 (2)
S4*B*	0.90285 (5)	0.08103 (6)	0.99898 (4)	0.0602 (2)
O1*B*	0.6048 (1)	0.0925 (1)	1.0313 (1)	0.0589 (5)
O2*B*	0.6553 (1)	−0.0060 (1)	0.9770 (1)	0.0698 (6)
N1*B*	0.4479 (2)	0.1220 (2)	0.9885 (1)	0.0429 (5)
N2*B*	0.6477 (2)	0.3335 (2)	0.9455 (2)	0.0709 (8)
N3*B*	0.9504 (1)	0.0435 (1)	1.1420 (1)	0.0490 (6)
C1*B*	0.4439 (2)	0.1931 (2)	1.0378 (2)	0.0481 (7)
C2*B*	0.4920 (2)	0.2643 (2)	1.0237 (2)	0.0572 (8)
C3*B*	0.4918 (2)	0.3331 (2)	1.0780 (2)	0.081 (1)
C4*B*	0.5221 (3)	0.3037 (3)	1.1579 (2)	0.092 (1)
C5*B*	0.4716 (3)	0.2337 (2)	1.1714 (2)	0.086 (1)
C6*B*	0.4724 (2)	0.1640 (2)	1.1177 (2)	0.0650 (9)
C7*B*	0.4244 (2)	0.1354 (2)	0.9059 (2)	0.0478 (7)
C8*B*	0.3390 (2)	0.1614 (2)	0.8777 (2)	0.0702 (9)
C9*B*	0.3150 (3)	0.1711 (3)	0.7934 (2)	0.102 (1)
C10*B*	0.3291 (3)	0.0925 (3)	0.7565 (2)	0.105 (2)
C11*B*	0.4150 (2)	0.0678 (3)	0.7845 (2)	0.083 (1)
C12*B*	0.4403 (2)	0.0587 (2)	0.8689 (2)	0.0569 (8)
C13*B*	0.6560 (2)	0.0618 (2)	1.0062 (2)	0.0487 (7)
C14*B*	0.7330 (1)	0.1110 (2)	1.0160 (2)	0.0427 (6)
C15*B*	0.6645 (2)	0.2544 (2)	0.9452 (2)	0.0519 (7)
C16*B*	0.5945 (3)	0.3727 (3)	0.8801 (3)	0.111 (2)
C17*B*	0.6794 (2)	0.3852 (2)	1.0106 (3)	0.101 (2)
C18*B*	0.8921 (2)	0.0662 (2)	1.0825 (2)	0.0417 (6)
C19*B*	0.9423 (2)	0.0357 (2)	1.2166 (2)	0.072 (1)
C20*B*	1.0292 (2)	0.0259 (2)	1.1361 (2)	0.080 (1)

Table 2. *Selected geometric parameters (Å, °)*

S1*A*—C14*A*	1.799 (3)	S1*B*—C14*B*	1.807 (3)
S1*A*—C15*A*	1.790 (3)	S1*B*—C15*B*	1.765 (3)
S2*A*—C15*A*	1.644 (3)	S2*B*—C15*B*	1.658 (3)
S3*A*—C14*A*	1.798 (3)	S3*B*—C18*B*	1.771 (3)
S3*A*—C18*A*	1.766 (3)	S3*B*—C14*B*	1.812 (3)
S4*A*—C18*A*	1.647 (3)	S4*B*—C18*B*	1.649 (3)
O1*A*—C13*A*	1.242 (3)	O1*B*—C13*B*	1.239 (3)
O2*A*—C13*A*	1.232 (3)	O2*B*—C13*B*	1.241 (3)
N1*A*—C1*A*	1.499 (4)	N1*B*—C1*B*	1.504 (4)
N1*A*—C7*A*	1.499 (4)	N1*B*—C7*B*	1.501 (3)
N2*A*—C15*A*	1.334 (3)	N2*B*—C15*B*	1.333 (4)
N2*A*—C16*A*	1.463 (4)	N2*B*—C17*B*	1.461 (5)
N2*A*—C17*A*	1.452 (4)	N2*B*—C16*B*	1.464 (5)
N3*A*—C18*A*	1.345 (4)	N3*B*—C18*B*	1.338 (3)
N3*A*—C19*A*	1.465 (5)	N3*B*—C19*B*	1.453 (4)
N3*A*—C20*A*	1.462 (5)	N3*B*—C20*B*	1.455 (4)
C13*A*—C14*A*	1.549 (3)	C13*B*—C14*B*	1.547 (4)
N1*A*···O1*A*	2.701 (3)	N1*B*···O1*B*	2.698 (3)
N1*A*···O2*A*$^{\rm i}$	2.796 (3)	N1*B*···O2*B*$^{\rm ii}$	2.837 (3)

C14A—S1A—C15A	103.8 (1)	C14B—S1B—C15B	103.4 (1)
C14A—S3A—C18A	101.8 (1)	C14B—S3B—C18B	104.0 (1)
C7A—N1A—C1A	117.6 (2)	C7B—N1B—C1B	118.2 (2)
C15A—N2A—C16A	119.9 (3)	C15B—N2B—C16B	120.9 (3)
C15A—N2A—C17A	124.3 (2)	C15B—N2B—C17B	122.6 (3)
C16A—N2A—C17A	115.7 (3)	C16B—N2B—C17B	116.5 (3)
C18A—N3A—C19A	123.0 (3)	C18B—N3B—C19B	124.4 (2)
C18A—N3A—C20A	120.5 (4)	C18B—N3B—C20B	121.0 (2)
C19A—N3A—C20A	116.4 (3)	C19B—N3B—C20B	114.6 (2)
N1A—C1A—C2A	111.9 (2)	N1B—C1B—C2B	111.5 (2)
N1A—C1A—C6A	108.9 (2)	N1B—C1B—C6B	107.6 (2)
N1A—C7A—C8A	108.2 (2)	N1B—C7B—C8B	110.9 (2)
N1A—C7A—C12A	111.2 (2)	N1B—C7B—C12B	108.8 (2)
O1A—C13A—O2A	127.3 (3)	O1B—C13B—O2B	128.2 (3)
O1A—C13A—C14A	114.7 (2)	O1B—C13B—C14B	117.0 (3)
O2A—C13A—C14A	118.0 (2)	O2B—C13B—C14B	114.7 (3)
C13A—C14A—S1A	107.2 (2)	C13B—C14B—S1B	116.6 (2)
C13A—C14A—S3A	113.2 (2)	C13B—C14B—S3B	105.5 (2)
S3A—C14A—S1A	108.3 (1)	S3B—C14B—S1B	103.4 (1)
N2A—C15A—S1A	112.4 (2)	N2B—C15B—S1B	113.4 (2)
N2A—C15A—S2A	124.9 (2)	N2B—C15B—S2B	124.3 (3)
S2A—C15A—S1A	122.8 (2)	S2B—C15B—S1B	122.3 (2)
N3A—C18A—S3A	113.0 (3)	N3B—C18B—S3B	112.2 (2)
N3A—C18A—S4A	124.3 (3)	N3B—C18B—S4B	124.4 (2)
S4A—C18A—S3A	122.7 (2)	S4B—C18B—S3B	123.4 (2)

Symmetry codes: (i) $-x, 1-y, 2-z$; (ii) $1-x, -y, 2-z$.

Data collection: *CAD*-4 *VAX/PC* (Enraf–Nonius, 1988). Cell refinement: *CAD*-4 *VAX/PC*. Data reduction: *Xtal*3.0 (Hall & Stewart, 1990). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ZORTEP* (Zsolnai & Pritzkow, 1994); *PLUTON* (Spek, 1994). Software used to prepare material for publication: *SHELXL*93.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: DE1009). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Domiano, P. & Branca, C. (1990). *Acta Cryst.* C**46**, 510–512.

Enraf–Nonius (1988). *CAD-4 VAX/PC Fortran System. Operator's Guide to the Enraf–Nonius CAD-4 Diffractometer Hardware, its Software and the Operating System.* Enraf–Nonius, Delft, The Netherlands.

Fawcett, C. H., Wain, R. L. & Wrightman, F. (1956). *Nature* (*London*), **178**, 972–974.

Hall, S. R. & Stewart, J. M. (1990). Editors. *Xtal*3.0 *Reference Manual.* Universities of Western Australia, Australia, and Maryland, USA.

Kerk, G. J. M. van der, van Raalte, M. H., Kaars Sijpesteijn, A. & van der Veen, R. (1955). *Nature* (*London*), **176**, 308–310.

Ng, S. W. (1992). *J. Crystallogr. Spectrosc. Res.* **22**, 615–618.

Ng, S. W. (1993). *J. Crystallogr. Spectrosc. Res.* **23**, 73–75.

Pluijgers, C. W. & van Der Kerk, G. J. M. (1961). *Recueil.* **80**, 1089–1100.

Sheldrick, G. M. (1985). *SHELXS*86. *Program for the Solution of Crystal Structures.* University of Göttingen, Germany.

Sheldrick, G. M. (1993). *SHELXL*93. *Program for Crystal Structure Refinement.* University of Göttingen, Germany.

Spek, A. L. (1994). *PLUTON. Molecular Graphics Program.* University of Utrecht, The Netherlands.

Zsolnai, L. & Pritzkow, H. (1994). *ZORTEP.* University of Heidelberg, Germany.

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7,7′-Bis[(aza-18-crown-6)carbonyl]thioindigo

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Abstract

The title compound, 7,7′-bis[(4,7,10,13,16-pentaoxa-1-azacyclooctadecane)carbonyl]thioindigo†, $C_{42}H_{54}N_2O_{14}S_2$, was found to be centrosymmetric and planar. Three members of the crown ether ring were disordered with roughly equal occupancy between two sets of positions.

Comment

Photoresponsive molecular hosts have received attention in the literature as light-controlled 'on–off switches' for supramolecular processes (Wyman & Brode, 1951; Kumar & Neckers, 1989). Azobenzene derivatives have been used to photoregulate enzyme activity (Westmark, Kelly & Smith, 1993), ion recognition and transport (Shinkai, Minami, Kusano & Manabe 1982), and membrane permeability (Aoyama, Watanabe & Inoue, 1990). Thioindigo derivatives have been studied as metal ion recognition and transport systems (Irie & Kato, 1985; Fatah-ur Rahman, Fukunishi, Kuwabara, Yamanaka & Nomura, 1993; Fatah-ur Rahman & Fukunishi, 1994), as dopants for photoresponsive media (Dinescu, Mezo, Luyt & Lemieux, 1994) and as materials for optical memory and switching (Saika, Iyoda, Honda & Shimidzu, 1992). We recently investigated the photochemistry of *N*,*N*′-diacylindigo dyes (Smith *et al.*, 1993, 1994). Our experience with indigo photochemistry and crowned recognition/transport systems (Bien, Shang & Smith, 1995) prompted us to prepare the title compound, (I), as a potential photoswitchable ionophore.

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† IUPAC: 1,2-dihydro-2-[1,3-dihydro-3-oxo-7-{(4,7,10,13,16-pentaoxa-1-azacyclooctadecane)carbonyl}-1-thio-2*H*-indol-2-ylidene]-7-[(4,7,10,13,16-pentaoxa-1-azacyclooctadecane)carbonyl]-1-thio-3*H*-indol-3-one.