$\omega/2\theta$ scans (rate: $6°$ min^{-1} in ω)
Absorption correction: none
6224 measured reflections
3112 independent reflections
2142 reflections with $I > 2\sigma(I)$

$h = -10 \rightarrow 10$
$k = -14 \rightarrow 14$
$l = -10 \rightarrow 10$
3 standard reflections every 100 reflections intensity variation: 0.50%

Refinement

Refinement on F^2
$R(F) = 0.035$
$wR(F^2) = 0.094$
$S = 1.008$
3112 reflections
220 parameters
H atoms riding
$w = 1/[\sigma^2(F_o^2) + (0.0363P)^2 + 0.1931P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.154$ e Å^{-3}
$\Delta\rho_{min} = -0.195$ e Å^{-3}
Extinction correction: *SHELXL97*
Extinction coefficient: 0.030 (3)
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

C11—C9'	1.792 (2)	C7'—C9'	1.535 (3)
C1'—C9	1.528 (2)	C7'—C8'	1.540 (3)
C2'—C7'	1.542 (2)	C7'—C10'	1.549 (3)
C1'—C2'—C7'	124.25 (15)	C6'—C1'—C9	115.04 (15)
C3'—C2'—C7'	119.13 (16)	C9'—C7'—C10'	108.03 (16)
C2'—C1'—C9	125.76 (15)	C9'—C7'—C8'	107.43 (15)
C4b—C8a—C9—C1'	-126.03 (16)	C9—C1'—C2'—C7'	5.2 (3)
C8—C8a—C9—C1'	56.6 (2)	C9—C1'—C6'—C5'	176.66 (17)
C1'—C9—C9a—C1	-54.2 (2)	C6'—C1'—C2'—C3'	2.2 (2)

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1996). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *PROCESS* in *TEXSAN* (Molecular Structure Corporation, 1995). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985) in *TEXSAN*. Program(s) used to refine structure: *LS* in *TEXSAN* and *SHELXL97* (Sheldrick, 1997). Molecular graphics: *ORTEP* (Johnson, 1965) in *TEXSAN*. Software used to prepare material for publication: *TEXSAN, SHELXL97* and *PLATON* (Spek, 1990).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1442). Services for accessing these data are described at the back of the journal.

References

Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.
Meyers, C. Y., Hou, Y., Lutfi, H. G., Robinson, P. D., Dunn, H. E. & Seyler, J. W. (1997). Am. Chem. Soc. Natl Meet., San Francisco, April 13–17, Abstract ORGN 351.
Molecular Structure Corporation (1995). *TEXSAN. Single Crystal Structure Analysis Software.* Version 1.7-1. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
Molecular Structure Corporation (1996). *MSC/AFC Diffractometer Control Software.* MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
Nakamura, M., Nakamura, N. & Ōki, M. (1977). *Bull. Chem. Soc. Jpn*, **50**, 1097–1101.
Robinson, P. D., Hou, Y., Lutfi, H. G. & Meyers, C. Y. (1998). *Acta Cryst.* C54, 73–77.
Schreiner, P. R., Schleyer, P. v. R. & Hill, R. K. (1993). *J. Org. Chem.* **58**, 2822–2829.
Sheldrick, G. M. (1985). *SHELXS86. Program for the Solution of Crystal Structures.* University of Göttingen, Germany.
Sheldrick, G. M. (1997). *SHELXL97. Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.
Spek, A. L. (1990). *Acta Cryst.* A46, C-34.

3,4-Bis(1-adamantyl)-1,2-dithiete: the First Structurally Characterized Dithiete Unsupported by a Ring or Benzenoid Frame

James P. Donahue and Richard H. Holm

Department of Chemistry and Chemical Biology, Harvard University, 12 Oxford Street, Cambridge, MA 01238, USA. E-mail: holm@chemistry.harvard.edu

Abstract

The structure determination of 3,4-bis(1-adamantyl)-1,2-dithiete, $(C_{10}H_{15})_2C_2S_2$ or $C_{22}H_{30}S_2$, reported herein is the first crystallographic characterization of a 1,2-dithiete molecule unsupported by a benzenoid frame. Two independent molecules exist in the asymmetric unit separated by a pseudo-inversion center. The S_2C_2 four-membered dithiete ring is planar, with a trapezoidal shape enforced by the longer disulfide bond [average 2.086 (2) Å] compared with the olefinic bond [average 1.363 (6) Å]. The adamantyl substituents differ from one another by adopting slightly different rotational conformations with respect to the dithiete ring. The quaternary C atoms of the adamantyl groups deviate only slightly from the plane of the dithiete ring (average displacement of 0.023 Å).

Comment

1,2-Dithietes and their valence tautomers, the α-dithiones (see scheme below), have long been known to add oxidatively to low-valent transition metal compounds to form redox-active bis- or tris(dithiolene) metal complexes $[M(S_2C_2R_2)_{2,3}]^z$, many examples of

which have been characterized (King, 1963; Davison *et al.*, 1964*a*,*b*; Kusters & de Mayo, 1974).

Generally prepared by reaction of elemental sulfur with the corresponding alkyne, 1,2-dithietes are comparatively rare molecules whose examples range from the reactive 3,4-bis(trifluoromethyl)-1,2-dithiete (Krespan, 1961) to the relatively unreactive electron-rich *tert*-butyl- and adamantyl-substituted versions (Krebs *et al.*, 1979; Choi *et al.*, 1993; Nakayama *et al.*, 1993). In at least one instance, a dithiete has been demonstrated to exist in solution equilibrium with a *trans*-α-dithione (Kusters & de Mayo, 1974). A dithiete has also been reported to be an intermediate in the transformation of disodium dimercaptomaleonitrile to tetracyano-1,4-dithiin (Simmons *et al.*, 1962). The only dithiete previously characterized crystallographically is 3β-acetoxy-6,7-epidithio-19-norlanosta-5,7,9,11-tetraene, in which the dithiete moiety is undoubtedly stabilized *vis-à-vis* the dithione by the conjugative stability of its aromatic frame (Boar *et al.*, 1975). The existence of dithiolene chelate rings in the co-factors of certain molybdenum and tungsten enzymes (Schindelin *et al.*, 1996; Chan *et al.*, 1995) has rekindled interest in the synthesis and properties of dithiolene ligands, their precursors, and their complexes. In the course of work on biologically-related dithiolene complexes, we became interested in electron-rich dithietes. We prepared 3,4-bis(1-adamantyl)-1,2-dithiete, (I), and confirmed its assignment as such by X-ray crystallography. This is the first structure of a dithiete unsupported by a benzenoid frame or other ring system.

(I)
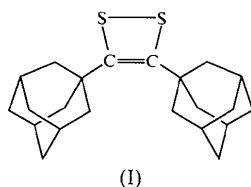
3,4-Bis(1-adamantyl)-1,2-dithiete crystallizes in space group $P2_12_12_1$ with two inequivalent, but metrically nearly identical, molecules (Table 1). We briefly describe molecule 1 (Fig. 1), which features an essentially planar C_2S_2 four-membered ring, the average deviation from the mean plane being 0.001 Å (Fig. 1). The S1—S2 bond length [2.087 (1) Å] is intermediate in length between that of the benzenoid dithiete (2.12 Å; Boar *et al.*, 1975) and bis(1-adamantyl) disulfide [2.048 (7) Å; Rindorf *et al.*, 1980]. It and the shorter olefinic C1—C2 bond [1.363 (4) Å] impose a trapezoidal shape on the ring, in which the average internal angles are 78.3 (1)

(C—S—S) and 101.7 (3)° (C—C—S). Atoms C3 and C4 of the adamantyl substituents are displaced from the dithiete mean plane by −0.091 (3) and 0.043 (3) Å, respectively, resulting in a torsion angle C3—C1—C2—C4 of 7.4°. This value contrasts with a similarly defined torsion angle of 84.4° in the structure of ring-opened 1,2-bis(1-adamantyl)ethane-1,2-dithione *S,S'*-dioxide, formed from this dithiete by oxidation with *m*-chloroperoxybenzoic acid (Nakayama *et al.*, 1995). As shown, the adamantyl groups differ conformationally in that one is rotated slightly with respect to the other. The net rotational difference between the adamantyl substituents is 7.6 (4)° for molecule 1, as defined by the difference in the C6—C3—C1—C2 [79.3 (4)°] and C15—C4—C2—C1 [71.7 (4)°] torsion angles. Molecule 2 has a similarly defined net rotational difference of 9.7 (6)° between the rotational conformations of its adamantyl groups [C29—C25—C23—C24 42.6 (5) and C38—C26—C24—C23 52.3 (4)°]. These rotational differences within and between each dithiete apparently contribute to disrupting a true inversion center between the independent molecules which would otherwise relate them. The structural parameters of the adamantyl substituents are closely comparable to those found in similar molecules (Donohue & Goodman, 1967; Alden *et al.*, 1968; Rindorf *et al.*, 1980).
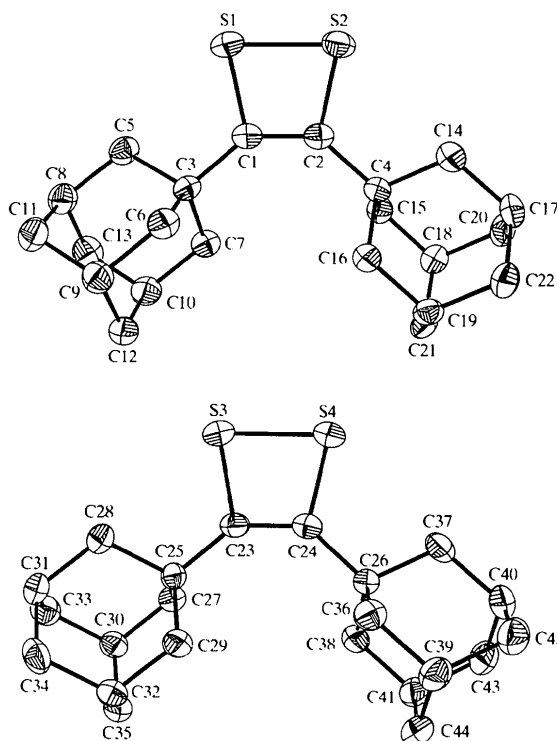

Fig. 1 *ORTEP* [in *SHELXTL/PC* (Sheldrick, 1995)] drawings of the two independent molecules of 3,4-bis(1-adamantyl)-1,2-dithiete showing 50% displacement ellipsoids. H atoms have been omitted for clarity.

Experimental

3,4-Bis(1-adamantyl)-1,2-dithiete was prepared and purified according to the literature method of Nakayama *et al.* (1993). Slow recrystallization of the chromatographed product from *n*-hexane at 277 K afforded crystals as pale-yellow plates. A suitable crystal was mounted on a glass fiber using grease.

Crystal data

$C_{22}H_{30}S_2$	Mo $K\alpha$ radiation
$M_r = 358.58$	$\lambda = 0.71073$ Å
Orthorhombic	Cell parameters from 358
$P2_12_12_1$	reflections
$a = 13.0470\,(2)$ Å	$\theta = 2.89\text{–}20.47°$
$b = 13.3683\,(1)$ Å	$\mu = 0.285$ mm^{-1}
$c = 21.4670\,(3)$ Å	$T = 213\,(2)$ K
$V = 3744.19\,(8)$ Å^3	Plate
$Z = 8$	$0.40 \times 0.30 \times 0.10$ mm
$D_x = 1.272$ Mg m^{-3}	Pale yellow
D_m not measured	

Data collection

Siemens CCD diffractometer	5164 reflections with
ω scans	$I > 2\sigma(I)$
Absorption correction:	$R_{int} = 0.088$
empirical from redundant	$\theta_{max} = 25°$
measurements (Blessing,	$h = -15 \rightarrow 15$
1995)	$k = -15 \rightarrow 15$
$T_{min} = 0.673$, $T_{max} = 0.972$	$l = -25 \rightarrow 13$
19 927 measured reflections	Intensity decay: $<1\%$
6592 independent reflections	

Refinement

Refinement on F^2	Extinction correction:
$R(F) = 0.045$	SHELXL93
$wR(F^2) = 0.094$	Extinction coefficient:
$S = 1.038$	0.0062 (5)
6592 reflections	Scattering factors from
674 parameters	*International Tables for*
All H atoms refined	*Crystallography* (Vol. C)
$w = 1/[\sigma^2(F_o^2) + (0.03P)^2]$	Absolute structure: Flack
where $P = (F_o^2 + 2F_c^2)/3$	(1983)
$(\Delta/\sigma)_{max} = -0.001$	Flack parameter = -0.08 (7)
$\Delta\rho_{max} = 0.28$ e Å^{-3}	
$\Delta\rho_{min} = -0.39$ e Å^{-3}	

Table 1. Selected geometric parameters (Å, °)

S1—C1	1.786 (3)	C1—C2	1.363 (4)
S1—S2	2.0869 (12)	C1—C3	1.527 (4)
S2—C2	1.784 (3)	C2—C4	1.522 (4)
S3—C23	1.791 (3)	C23—C24	1.362 (4)
S3—S4	2.0841 (11)	C23—C25	1.512 (4)
S4—C24	1.786 (3)	C24—C26	1.525 (4)
C1—S1—S2	78.40 (10)	C24—C23—C25	138.9 (2)
C2—S2—S1	78.20 (10)	C24—C23—S3	101.3 (2)
C23—S3—S4	78.45 (10)	C25—C23—S3	119.5 (2)
C24—S4—S3	78.25 (10)	C23—C24—C26	137.3 (3)
C2—C1—C3	138.9 (2)	C23—C24—S4	102.0 (2)
C2—C1—S1	101.5 (2)	C26—C24—S4	120.7 (2)
C3—C1—S1	119.4 (2)	C23—C25—C28	109.4 (2)
C1—C2—C4	137.3 (3)	C23—C25—C29	113.3 (2)
C1—C2—S2	101.9 (2)	C23—C25—C27	109.9 (2)
C4—C2—S2	120.7 (2)	C24—C26—C38	111.8 (2)
C1—C3—C5	109.3 (2)	C24—C26—C37	109.9 (2)
C1—C3—C7	112.9 (2)	C24—C26—C36	110.1 (2)
C1—C3—C6	109.7 (2)		

Data were collected with a Siemens (Bruker) SMART CCD area-detector instrument equipped with an LT-2 low temperature apparatus operating at 213 K. Data were measured using ω scans of 3° per frame with 60 s frames such that 1271 frames were collected for a hemisphere of data. The first 50 frames were recollected at the end of data collection to monitor for decay. Data collection was cut at a 2θ value of 50° for a final resolution of 0.84 Å. The structure was solved in $P2_12_12_1$ by analysis of systematic absences. All non-H atoms were refined anisotropically. All H atoms were located in the final electron-density maps, named, and refined isotropically. The crystal showed no decomposition during data collection.

Cell parameters were retrieved using *SMART* software (Siemens, 1995a) and refined using *SAINT* software (Siemens, 1995b) on all observed reflections between 2θ of 3 and 50°. Data reduction and integration were performed using the *SAINT* software, which corrects for Lorentz–polarization and decay. Absorption corrections were applied using the program *SADABS* (Sheldrick, 1995) based on the method of Blessing (1995). The structure was solved by direct methods using *SHELXS97* (Sheldrick, 1990) and refined by least squares on F^2 using *SHELXL97* (Sheldrick, 1997) incorporated in *SHELXTL/PC* (Siemens, 1995c), which was also used for the molecular graphics and the preparation of material for publication.

References

Alden, R. A., Kraut, J. & Traylor, T. G. (1968). *J. Am. Chem. Soc.* **90**, 74–82.

Blessing, R. H. (1995). *Acta Cryst.* A51, 33–38.

Boar, R. B., Hawkins, D. W., McGhie, J. F., Misra, S. C., Barton, D. H. R., Ladd, M. F. C. & Povey, D. C. (1975). *J. Chem. Soc. Chem. Commun.* p. 756.

Chan, M. K., Mukund, S., Kletzin, A., Adams, M. W. W. & Rees, D. C. (1995). *Science*, **267**, 1463–1469.

Choi, K. S., Akiyama, I., Hoshino, M. & Nakayama, J. (1993). *Bull. Chem. Soc. Jpn*, **66**, 623–629.

Davison, A., Edelstein, N., Holm, R. H. & Maki, A. H. (1964a). *Inorg. Chem.* **3**, 814–823.

Davison, A., Edelstein, N., Holm, R. H. & Maki, A. H. (1964b). *J. Am. Chem. Soc.* **86**, 2799–2805.

Donohue, J. & Goodman, S. H. (1967). *Acta Cryst.* **22**, 352–354.

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

King, R. B. (1963). *Inorg. Chem.* **2**, 641–642.

Krebs, A., Colberg, H., Höpfner, U., Kimling, H. & Odenthal, J. (1979). *Heterocycles*, **12**, 1153–1156.

Krespan, C. G. (1961). *J. Am. Chem. Soc.* **83**, 3434–3437.

Kusters, W. & de Mayo, P. (1974). *J. Am. Chem. Soc.* **96**, 3502–3511.

Nakayama, J., Choi, K. S., Akiyama, I. & Hoshino, M. (1993). *Tetrahedron Lett.* **34**, 115–118.

Nakayama, J., Mizumura, A., Yokomori, A., Krebs, A. & Schütz, K. (1995). *Tetrahedron Lett.* **36**, 8583–8586.

Rindorf, G., Jørgensen, F. S. & Snyder, J. P. (1980). *J. Org. Chem.* **45**, 5343–5347.

Schindelin, H., Kisker, C., Hilton, J., Rajagopalan, K. V. & Rees, D. C. (1996). *Science*, **272**, 1615–1621.

Sheldrick, G. M. (1990). *SHELXS97. Program for the Solution of Crystal Structures*. University of Göttingen, Germany.

Sheldrick, G. M. (1995). *SADABS. Program for Empirical Absorption Correction*. University of Göttingen, Germany.

Sheldrick, G. M. (1997). *SHELXL97. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.

Siemens (1995a). *SMART*. Version 4.043. *Software for the CCD Detector System*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Siemens (1995b). *SAINT*. Version 4.035. *Software for the CCD Detector System*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Siemens (1995c). *SHELXTL/PC*. Release 5.03. *Program Library for Structure Solution and Molecular Graphics*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Simmons, H. E., Blomstrom, D. C. & Vest, R. D. (1962). *J. Am. Chem. Soc.* **84**, 4772–4781.

8-Aminoquinolinium Chloride Dihydrate

BARRY J. PRINCE[a] AND MARK M. TURNBULL[b]

[a]*Department of Chemistry, University of Canterbury, Christchurch, New Zealand, and* [b]*Carlson School of Chemistry, Clark University, 950 Main St., Worcester, MA 01610, USA. E-mail: mturnbull@clarku.edu*

Abstract

The title compound, $C_9H_9N_2^+.Cl^-.2H_2O$, crystallized from water as pale-orange plates. The structure reveals strong hydrogen bonding between one of the water molecules and both the quinolinium [N—H···O 2.691 (4) Å] and amino [N—H···O 2.967 (4) Å] H atoms. The second water molecule is hydrogen bonded to the first [O—H···O 2.658 (3) Å], and weakly to two different chloride ions. The overall packing results in stacks of quinolinium ions, with adjacent molecules having opposite orientations.

Comment

We are interested in the magnetic behavior of compounds with the general formula $(AH)_2MX_4$, where A is an organic base, M is a 2+ transition metal ion and X is a halide. Previous work by ourselves (Albrecht *et al.*, 1998) and others (Place & Willett, 1987*a,b*; Luque *et al.*, 1997) has shown that these compounds may pack in such a fashion as to yield low-dimensional magnetic lattices, where the magnetic exchange is mediated by van der Waals contacts between the halides. The nature of the packing is determined by the size and shape of

the organic base. Examination of the structures of the hydrohalide salts of these bases has sometimes proved useful in predicting which will generate useful magnetic lattices (Prince & Turnbull, 1996; Anagnostis & Turnbull, 1998). The study of the structure of 8-aminoquinolinium chloride dihydrate, (I), was undertaken for this purpose.

(I)
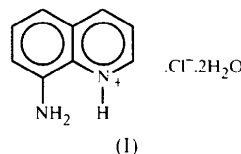
8-Aminoquinolinium chloride crystallized from water as the dihydrate in the space group $P\bar{1}$. The molecular structure is shown in Fig. 1. The quinolinium ring is planar, with the ring atoms and the amino group having a mean deviation from the plane of 0.011 (1) Å. The bond lengths within the ring are all 1.39 ± 0.03 Å, except for the short N1—C2 bond of 1.319 (3) Å. The short bond to the amino nitrogen, 1.354 (3) Å, reflects a strong π-character on N2—C8. Similarly, the bond angles within the ring are all $120\pm3°$, except for the enlarged C9—N1—C2 angle [123.7 (2)°] and the reduced C7—C8—C9 angle [116.3 (2)°]. The bond lengths and angles within the quinolinium ring are, in general, comparable with those reported for the dimeric silver coordination complex (Schmidbauer *et al.*, 1991). The bond lengths are also comparable with those reported for the aqua-bis(8-aminoquinoline)zinc tetrachlorozincate salt (Kerr *et al.*, 1981), while the angles only deviate significantly near the atoms involved in chelating the zinc ion (N1, C8 and C9 in the present structure). A third coordination complex of 8-aminoquinoline, involving nickel, has also been reported (Mohedano *et al.*, 1985), but comparisons there are not useful as that complex shows substantial distortions of the quinoline ring.
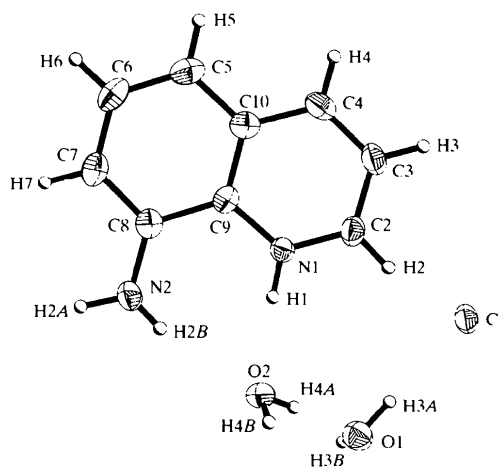

Fig. 1. The molecular structure of 8-aminoquinolinium chloride dihydrate, showing displacement ellipsoids at 50% probability.