Data collection

MacScience MXC3 diffractometer	$\theta_{max} = 26.43°$
$\theta/2\theta$ scans	$h = 0 \rightarrow 14$
Absorption correction: none	$k = -20 \rightarrow 0$
3595 measured reflections	$l = -10 \rightarrow 10$
2855 independent reflections	3 standard reflections
2217 reflections with	every 100 reflections
$I > 2\sigma(I)$	intensity decay: not
$R_{int} = 0.028$	significant

Refinement

Refinement on F	$(\Delta/\sigma)_{max} = 0.009$
$R = 0.061$	$\Delta\rho_{max} = 0.24$ e Å^{-3}
$wR = 0.063$	$\Delta\rho_{min} = -0.29$ e Å^{-3}
$S = 1.316$	Extinction correction: none
2217 reflections	Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)
262 parameters	
All H atoms refined	
$w = 1/[\sigma^2(F_o) + 0.001F_o^2]$	

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

O1—C1	1.217 (3)	O7—C14	1.359 (2)
O2—C4	1.211 (3)	C1—C2	1.482 (3)
O3—C5	1.332 (2)	C1—C14	1.477 (3)
O3—C6	1.448 (2)	C2—C3	1.309 (4)
O4—C7	1.400 (3)	C3—C4	1.461 (3)
O4—C8	1.416 (3)	C4—C5	1.504 (3)
O5—C9	1.406 (3)	C5—C14	1.345 (3)
O5—C10	1.420 (3)	C6—C7	1.491 (3)
O6—C11	1.412 (3)	C8—C9	1.484 (3)
O6—C12	1.401 (3)	C10—C11	1.468 (4)
O7—C13	1.457 (3)	C12—C13	1.486 (3)
C5—O3—C6	122.2 (2)	O3—C5—C14	130.1 (2)
C7—O4—C8	116.4 (2)	C4—C5—C14	120.0 (2)
C9—O5—C10	113.8 (2)	O3—C6—C7	106.3 (2)
C11—O6—C12	113.0 (2)	O4—C7—C6	113.5 (2)
C13—O7—C14	118.2 (2)	O4—C8—C9	112.6 (2)
O1—C1—C2	120.7 (2)	O5—C9—C8	109.2 (2)
O1—C1—C14	120.9 (2)	O5—C10—C11	108.2 (2)
C2—C1—C14	118.3 (2)	O6—C11—C10	108.5 (2)
C1—C2—C3	121.2 (2)	O6—C12—C13	108.7 (2)
C2—C3—C4	121.2 (2)	O7—C13—C12	107.7 (2)
O2—C4—C3	121.2 (2)	O7—C14—C1	117.6 (2)
O2—C4—C5	120.4 (2)	O7—C14—C5	122.2 (2)
C3—C4—C5	118.4 (2)	C1—C14—C5	119.8 (2)
O3—C5—C4	109.9 (2)		
C6—O3—C5—C4	178.2 (2)	C2—C1—C14—C5	-12.2 (2)
C5—O3—C6—C7	-178.5 (2)	C1—C2—C3—C4	-1.7 (2)
C6—O3—C5—C14	-1.3 (2)	C2—C3—C4—O2	177.1 (3)
C8—O4—C7—C6	111.3 (2)	C2—C3—C4—C5	-4.7 (2)
C7—O4—C8—C9	-99.6 (2)	O2—C4—C5—O3	1.2 (2)
C10—O5—C9—C8	-179.0 (3)	O2—C4—C5—C14	-179.3 (3)
C9—O5—C10—C11	171.3 (3)	C3—C4—C5—O3	-177.0 (2)
C12—O6—C11—C10	168.1 (3)	C3—C4—C5—C14	2.5 (2)
C11—O6—C12—C13	178.6 (2)	O3—C5—C14—O7	-2.6 (2)
C13—O7—C14—C1	-48.6 (2)	O3—C5—C14—C1	-174.6 (3)
C13—O7—C14—C5	139.2 (2)	C4—C5—C14—O7	178.0 (3)
C14—O7—C13—C12	-142.3 (2)	C4—C5—C14—C1	6.0 (2)
O1—C1—C2—C3	-169.0 (3)	O3—C6—C7—O4	72.3 (2)
O1—C1—C14—O7	-5.5 (2)	O4—C8—C9—O5	67.4 (2)
O1—C1—C14—C5	166.9 (3)	O5—C10—C11—O6	-67.5 (2)
C2—C1—C14—O7	175.4 (3)	O6—C12—C13—O7	69.8 (2)
C14—C1—C2—C3	10.1 (2)		

Data collection: *CRYSTAN* (Edwards *et al.*, 1995). Cell refinement: *CRYSTAN*. Data reduction: *CRYSTAN*. Program(s) used to solve structure: *CRYSTAN*. Program(s) used to refine structure: *CRYSTAN*. Molecular graphics: *CRYSTAN*. Software used to prepare material for publication: *CRYSTAN*.

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New Examples of Donor–Acceptor Conjugated Systems Involving the 1,3-Dithiole Moiety

VLADIMIR KHODORKOVSKY, ARKADY ELLERN AND VADIM MOLDAVSKY

Chemistry Department, Ben-Gurion University of the Negev, PO Box 653, Beer-Sheva, Israel. E-mail: ellern@bgumail. bgu.ac.il

### Abstract

The crystal structures of 6-(4,5-dimethyl-2*H*-1,3-dithiol-2-ylidene)-6,7-dihydro-5*H*-dibenzo[*a,c*]cycloheptene-5,7-dione, $C_{20}H_{14}O_2S_2$, and 6-(4,5,6,7-tetrahydro-2*H*-1,3-benzodithiol-2-ylidene)-6,7-dihydro-5*H*-dibenzo[*a,c*]cycloheptene-5,7-dione, $C_{22}H_{16}O_2S_2$, have been determined. Strong intramolecular interactions are observed between the carbonyl groups of the seven-membered ring and the S atoms of the 1,3-dithiole ring.

Comment

In the course of our investigations on donor–acceptor conjugated systems involving the 1,3-dithiole moiety, we have determined the crystal structure of 2-(4,5-ethylenedithio-1,3-dithiol-2-ylidene)-1,3-indandione, (I) (Bulgarovskaya *et al.*, 1988). Strong intramolecular interactions between the carbonyl groups of the planar 1,3-indandione moiety and S atoms of the planar 1,3-dithiole moiety are considered to be responsible for the coplanarity of both moieties [see also Watson *et al.*

(1984)]. However, seven-membered cyclic 1,3-diketones should be non-planar. To the best of our knowledge, no crystal structure data on 6,7-dihydro-5H-dibenzo[a,c]-cycloheptene-5,7-dione derivatives have been reported previously. We report here on the crystal structures of two further analogues of (I), namely, 6-(4,5-dimethyl-2H-1,3-dithiol-2-ylidene)-6,7-dihydro-5H-dibenzo[a,c]-cycloheptene-5,7-dione, (II), and 6-(4,5,6,7-tetrahydro-2H-1,3-benzodithiol-2-ylidene)-6,7-dihydro-5H-dibenzo-[a,c]cycloheptene-5,7-dione, (III).

(I)

(II)   (III)
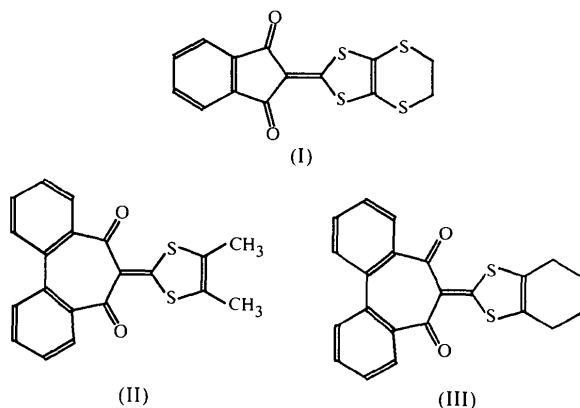
Compound (II) (Fig. 1) crystallizes in space group C2/c with half of the molecule in the asymmetric unit; the molecule has exact twofold rotation symmetry. The moiety involving the 1,3-dithiole ring and the C4 atom of the cycloheptene ring is almost planar (r.m.s. deviation 0.012 Å), and the carbonyl O atoms are displaced from this plane by 0.116 (4) Å on opposite sides. The interplanar angles between this plane and the benzene rings are 43.26 (8)°. The most interesting feature within this structure is the extremely strong intramolecular interaction between the carbonyl O atom and the S atom. The S· · ·O distance is 2.564 (3) Å, about 0.3 Å shorter than that found in 2-(1,3-dithiol-2-ylidene)-1,3-cyclopentenedione (Watson *et al.*, 1984), compound (I) (Bulgarovskaya *et al.*, 1988) and 2-(1,3-dithiolan-4-en-2-ylidene)-1,3-indandione (Bulgarovskaya *et al.*, 1990), and approximately equal to the distance found in diisopropyl 1,3-dithiol-2-ylidenemalonate (Vega & Baggio, 1989), where the carbonyl groups do not belong to any ring and are therefore subject to no steric constraints. The observed S· · ·O distance is significantly shorter then the sum of van der Waals radii of sulfur and oxygen (1.80 and 1.52 Å, respectively; Bondi, 1964).

No particularly short intermolecular contacts are found in the crystal of (II) and all S· · ·S distances are longer then 4.0 Å.

Compound (III) also crystallizes in space group C2/c, with Z = 12 (one and a half molecules in the asymmetric unit), although the unit-cell γ angle was consistently found to deviate markedly (*e.g.* > 0.6°) from 90°.
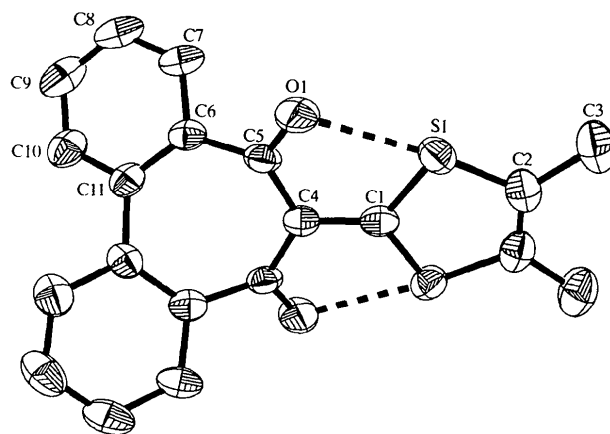

Fig. 1. The molecular structure of (II) showing 50% probability displacement ellipsoids.

The geometrical parameters of both molecules (one is in a general position and the other lies on a twofold axis) are essentially the same. As expected, the molecular geometry of (III) (Fig. 2) is very similar to that of (II). The moiety consisting of 1,3-dithiole and the C8 atom of the cycloheptene ring is planar (r.m.s. deviation of 0.004 Å for both crystallographically independent molecules), and the carbonyl O atoms are displaced by 0.141 (6)–0.219 (6) Å to either side of the plane. The interplanar angles between these planes and the benzene rings are 49.1 (1)–55.1 (1)°. The S· · ·O intramolecular distances in (III) were found to be close to those found in (II) [2.564 (4)–2.614 (4) Å]. In contrast to compound (II), short S· · ·S intermolecular contacts are found in the crystal structure of (III), with distances of 3.612 (4) and 3.714 (4) Å.
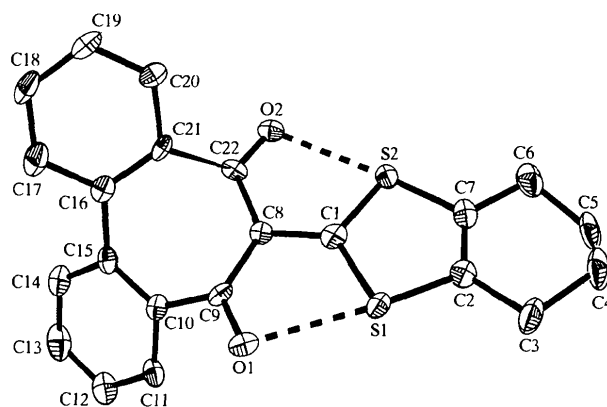

Fig. 2. The structure of the molecule of (III), in a general position, showing 50% probability displacement ellipsoids.

In conclusion, the presence of shortened intramolecular S· · ·O contacts within this group of compounds can hardly be explained by steric factors, and electronic interactions such as non-bonded resonance interactions

[see, for example, Klingsberg (1963)] should be taken into account.

Experimental

Derivatives (II) and (III) were synthesized from 6,7-dihydro-5H-dibenzo[a,c]cycloheptene-5,7-dione (Ried & Conte, 1971) and substituted 1,3-dithiol-2-immonium perchlorates (Campaign & Jacobsen, 1964). 6,7-Dihydro-5H-dibenzo[a,c]cyclo-heptene-5,7-dione (0.222 g, 1 mmol) and 1 mmol of the corresponding 1,3-dithiol-2-immonium perchlorate were dissolved in hot acetonitrile (30 ml), and triethylamine (0.28 ml, 2 mmol) was added in one portion. The reaction mixture was refluxed for 10 min and stirred at room temperature for 1 h. The yellow–brown precipitate was filtered and washed with water. The yields were 87 and 84% for crude (II) and (III), respectively. Single crystals of both compounds were grown from acetonitrile.

Compound (II)

Crystal data

$C_{20}H_{14}O_2S_2$
$M_r = 350.43$
Monoclinic
$C2/c$
$a = 16.600\,(3)$ Å
$b = 13.120\,(3)$ Å
$c = 7.960\,(2)$ Å
$\beta = 109.23\,(3)°$
$V = 1636.9\,(6)$ Å^3
$Z = 4$
$D_x = 1.422$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 38 reflections
$\theta = 8-15°$
$\mu = 0.334$ mm^{-1}
$T = 293\,(2)$ K
Block
$0.46 \times 0.33 \times 0.20$ mm
Yellow

Data collection

Syntex P$\bar{1}$ diffractometer
$\omega-2\theta$ scans
Absorption correction: none
3199 measured reflections
1640 independent reflections
853 reflections with
  $I > 2\sigma(I)$
$R_{int} = 0.051$

$\theta_{max} = 26.95°$
$h = 0 \rightarrow 20$
$k = -16 \rightarrow 16$
$l = -9 \rightarrow 9$
2 standard reflections
  every 98 reflections
  intensity decay: 4%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.043$
$wR(F^2) = 0.099$
$S = 0.969$
1640 reflections
110 parameters
H atoms riding
$w = 1/[\sigma^2(F_o^2) + (0.056P)^2]$
  where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.008$
$\Delta\rho_{max} = 0.184$ e Å^{-3}
$\Delta\rho_{min} = -0.257$ e Å^{-3}
Extinction correction: none
Scattering factors from
  International Tables for
  Crystallography (Vol. C)

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

S1—C1	1.684 (3)	C4—C5	1.418 (3)
C1—C4	1.400 (6)	C5—O1	1.200 (3)
S1—C1—S1^i	111.2 (3)	O1—C5—C6	119.0 (3)
C5^i—C4—C5	123.2 (4)	C4—C5—C6	121.8 (3)
O1—C5—C4	118.3 (3)		

Symmetry code: (i) $1 - x, y, \frac{1}{2} - z$.

Compound (III)

Crystal data

$C_{22}H_{16}O_2S_2$
$M_r = 376.47$
Monoclinic
$C2/c$
$a = 10.519\,(2)$ Å
$b = 25.456\,(5)$ Å
$c = 20.319\,(4)$ Å
$\beta = 92.03\,(3)°$
$V = 5437.4\,(18)$ Å^3
$Z = 12$
$D_x = 1.380$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 38 reflections
$\theta = 10-18°$
$\mu = 0.307$ mm^{-1}
$T = 293\,(2)$ K
Block
$0.51 \times 0.33 \times 0.28$ mm
Yellow–orange

Data collection

Syntex P$\bar{1}$ diffractometer
$\omega-2\theta$ scans
Absorption correction: none
6534 measured reflections
3229 independent reflections
2269 reflections with
  $I > 2\sigma(I)$
$R_{int} = 0.080$

$\theta_{max} = 22.16°$
$h = -11 \rightarrow 0$
$k = -26 \rightarrow 26$
$l = -21 \rightarrow 21$
2 standard reflections
  every 98 reflections
  intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.059$
$wR(F^2) = 0.132$
$S = 1.121$
3220 reflections
353 parameters
H atoms riding
$w = 1/[\sigma^2(F_o^2) + (0.07P)^2$
  $+ 14P]$
  where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.005$
$\Delta\rho_{max} = 0.574$ e Å^{-3}
$\Delta\rho_{min} = -0.371$ e Å^{-3}
Extinction correction: none
Scattering factors from
  International Tables for
  Crystallography (Vol. C)

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

S1—C1	1.740 (5)	C22—O2	1.232 (6)
S2—C1	1.723 (6)	S1′—C1′	1.727 (4)
C1—C8	1.415 (7)	C1′—C5′	1.407 (10)
C8—C9	1.449 (7)	C5′—C6′	1.455 (6)
C8—C22	1.455 (7)	C6′—O1′	1.237 (6)
C9—O1	1.242 (6)		
S2—C1—S1	113.7 (3)	C8—C22—C21	120.2 (4)
C9—C8—C22	125.1 (4)	S1″—C1′—S1′	114.8 (4)
O1—C9—C8	120.8 (4)	C6″—C5′—C6′	124.8 (6)
O1—C9—C10	118.0 (5)	O1′—C6′—C5′	121.1 (5)
C8—C9—C10	120.1 (4)	O1′—C6′—C7′	118.4 (4)
O2—C22—C8	120.8 (5)	C5′—C6′—C7′	119.6 (4)
O2—C22—C21	118.3 (5)		

Symmetry code: (i) $1 - x, y, \frac{1}{2} - z$.

For (III), the high-angle data were very weak and the data set was curtailed at $\theta = 22.16°$. Some highly anisotropic displacement parameters in the structure of (III) may indicate disorder, but this could not be resolved.

For both compounds, data collection: P3 (Siemens, 1990); cell refinement: P3; data reduction: P3; program(s) used to solve structures: SHELXS86 (Sheldrick, 1990); program(s) used to refine structures: SHELXL93 (Sheldrick, 1993); molecular graphics: SHELXTL (Siemens, 1992).

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1:1 Complex of Octadecanoic Acid and 3-Pyridinecarboxamide

Makoto Amai,[a] Tomohiro Endo,[a] Hiromasa Nagase,[a] Haruhisa Ueda[a] and Masayuki Nakagaki[b]

[a]*Department of Physical Chemistry, Hoshi University, 4-41 Ebara 2-Chome, Shinagawa-ku, Tokyo 142, Japan, and* [b]*Tokyo Institute of Colloid Science, 502 Higashi-Nakano 4-4-3, Nakano-ku, Tokyo 164, Japan. E-mail: ueda@hoshi.ac.jp*

Abstract

An equimolar mixture of stearic acid (octadecanoic acid) and nicotinamide (3-pyridinecarboxamide) in acetone yields crystals of a 1:1 complex, $C_{18}H_{36}O_2 \cdot C_6H_6N_2O$. In this structure, the 1:1 complexes form dimers through hydrogen bonds between the amide groups, thus forming a lamellar structure. The alkyl chain of stearic acid has an all-*trans* conformation.

Comment

The title compound, (I), has the bitter taste of nicotinamide and the pharmaceutical advantage of improved hygroscopicity (Ayukawa *et al.*, 1986). Nicotinamide is released from (I) at a certain temperature and pH level depending on the number of C atoms contained in the fatty acid. The applicability of a pH- and thermoresponsive drug delivery system has been reported (Yokoyama *et al.*, 1993; Yokoyama, Sunohara *et al.*, 1994; Yokoyama, Miyamura & Fujie, 1994). However, the crystal structures of these complexes have not been determined. Therefore, we report here the structure of the title compound, (I).

(I)
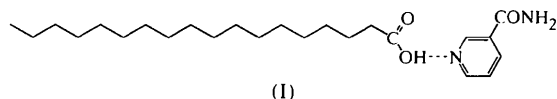
The numbering scheme for the equimolar complex of stearic acid and nicotinamide is given in Fig. 1. The equimolar complex forms a hydrogen-bonded dimer, thus forming a lamellar structure. As is apparent from Table 2, which gives geometric details of the hydrogen bonds, and also from Fig. 2, which shows a projection of the title compound along the *a* axis, three types of hydrogen bonding occur in this structure. One hydrogen bond forms between the N1 atom of the pyridine ring of the nicotinamide (acceptor) and the O2 atom of the stearic acid (donor), with an N1···O2 distance of 2.693 (1) Å. Another hydrogen bond forms between the O3 atom of the amide group of the nicotinamide (acceptor) and the N2 atom of the amide group of the other nicotinamide (donor), with an O3···N2[i] distance of 2.939 (1) Å, thus forming the dimer. The third hydrogen bond is formed between two amide groups, between atoms O3 (acceptor) and N2 (donor), with an O3···N2[ii] distance of 2.904 (1) Å, being parallel to the lamellar structures (the symmetry codes are as in Table 2).

As is apparent from Table 1, which gives bond lengths and torsion angles, the C1—O1 bond length of 1.199 (2) Å and the C1—O2 length of 1.321 (2) Å are characteristic of C=O and C—O bonds.

The amide group in the title compound is twisted out of the plane of the pyridine ring. The torsion angles N2—C24—C20—C21 and O3—C24—C20—C19 are 26.0 (2) and 25.3 (2)°, respectively; these angles are considerably different from the torsion angles of 179 and −168° calculated by Wright & King (1954). Compared with the crystal structure of nicotinamide alone, the amide group of the title compound is rotated in a counterclockwise direction by about 150° around C20—C24. That is to say, in the case of nicotinamide alone, two N atoms of the amide group and the pyridine ring are present on the same side, but in the title compound, the two N atoms are present on opposite sides.