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

O1—C11	1.225 (3)	O2—C11	1.254 (3)
C2—N1—C9	122.7 (2)	O1—C11—O2	126.4 (2)
C3—C4—C11	119.3 (2)	O1—C11—C4	117.2 (2)
C10—C4—C11	120.9 (2)	O2—C11—C4	116.4 (2)

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O2[i]	0.93 (2)	1.76 (3)	2.688 (2)	174 (2)
O3—H9···O1	0.81 (3)	2.04 (3)	2.852 (3)	177 (3)
O3—H10···O1[ii]	1.03 (4)	1.81 (4)	2.797 (3)	159 (3)
O4—H11···O2	0.87 (3)	1.98 (3)	2.837 (2)	169 (4)
O4—H12···O4[iii]	0.82 (3)	1.98 (3)	2.794 (2)	173 (4)
C2—H2···O3[iv]	0.98	2.19	3.165 (3)	171
C3—H3···O3[v]	0.98	2.40	3.318 (3)	156

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

Table 3. *First- and basic second-level graph-set descriptors involving hydrogen bonds which are designated a–e in the order given in Table 2*

	a	b	c	d	e
a	C(7)	$D_3^3(14)$	$D_3^3(14)$	$D_2^1(5)$	none
b		D	$C_2^1(4)$	$D_2^2(7)$	none
c			D	$D_2^2(7)$	none
d				D	$D_3^4(7)$
e					C(2)

Scan widths were $(1.60 + 0.35\tan\theta)°$ in ω, with a background/scan time-ratio of 0.5. The data were corrected for Lorentz and polarization effects. The Laue group assignment, systematic absences and the lack of centrosymmetry indicated by the intensity statistics led to assignment of the space group as Cc (No. 9); since refinement proceeded well, it was adopted. Difference Fourier methods were used to locate the initial H-atom positions. Initially, all H atoms were refined; the six C—H distances ranged from 0.91 (2) to 1.03 (2) Å. Subsequently, these six H atoms were made canonical with C—H = 0.98 Å and B_{iso} = 1.2 × B_{eq} of the attached C atom. Refined N—H and O—H distances are given in Table 2. The maximum effect of extinction is 5.9% of F_o for 15$\bar{1}$. Assignment of the absolute configuration was not possible. The maximum peak in the final difference map occurred ∼0.6 Å from C4; the maximum negative peak ∼0.6 Å from C11.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1995). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *TEXSAN*. Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *TEXSAN* and *PLATON* (Spek, 1990).

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Network of C—H···O interactions in 1,2-naphthalenedicarboxylic anhydride

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Abstract

The title substance, $C_{12}H_6O_3$, crystallized in the centrosymmetric space group $P2_1/c$ with one molecule in the asymmetric unit. Four significant C—H···O interactions have C···O distances ranging from 3.313 (2) to 3.453 (2) Å. They link each molecule directly to eight neighbors, generating a three-dimensional network. The anhydride group is compared with those in phthalic anhydride and 1,4,5,8-naphthalenetetracarboxylic 1,8:4,5-dianhydride.

Comment

Although conventional hydrogen bonds are not possible in 1,2-naphthalenedicarboxylic anhydride, (I), it is of interest in terms of C—H···O interactions since it possesses three potential acceptors, O1–O3, and six

potential H atom donors, C3–C8, per molecule. It crystallized in the centrosymmetric space group $P2_1/c$ with one molecule in the asymmetric unit. The refined molecule, with our numbering scheme, is shown in Fig. 1. In this structure the four leading intermolecular C—H$\cdots$O interactions have H$\cdots$O separations which are less than the corresponding sum of Bondi (1964) van der Waals radii. Their geometric parameters are given in
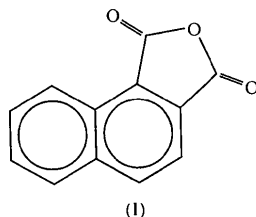

(I)

Table 2. These interactions, labeled a–d in the order in which they appear in Table 2, involve all the potential O-atom acceptors and four (of the potential six) C-atom donors, and link a central molecule directly to eight neighboring molecules as shown in Fig. 2. The results of graph-set analysis (Bernstein et al., 1995) for first- and basic second-level graphs are given in Table 3. Chains dominate these graphs; in their order of appearance in Table 3, these propagate along a, c, b, b, [201], b, a, and b. Clearly, these interactions generate a three-dimensional network. While the two tabulated rings are not developed in Fig. 2, three others are developed: a (complex) second-level ac ring with descriptor $R_4^2(23)$ and two third-level acd rings with descriptors $R_3^3(13)$ and $R_3^3(16)$.
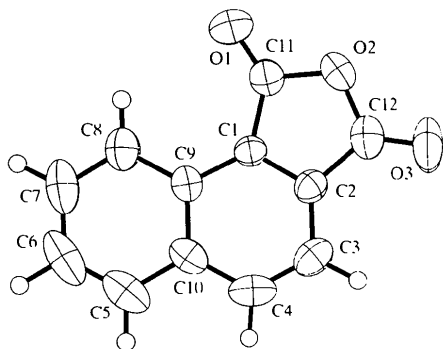

Fig. 1. ORTEPII (Johnson, 1976) drawing of (I), showing our numbering scheme. Displacement ellipsoids are drawn for 50% probability for all non-H atoms; spheres of arbitrary small radii depict H atoms.

In this structure, the 15 non-H atoms lie very nearly in a plane: the maximum deviation of any of these atoms from the best-fit plane describing them is 0.014 (2) Å, while the r.m.s. deviation is 0.005 (2) Å. Since, further, the dihedral angle between the two sets of non-parallel core planes is only 0.41 (4)°, all the molecular planes are either strictly or essentially parallel to one another. This structural feature is apparent in Fig. 2.
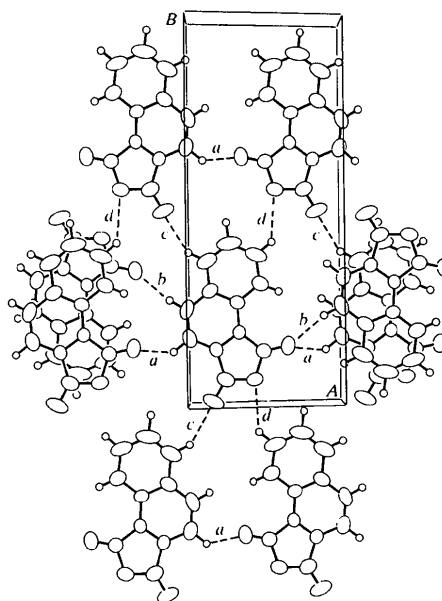

Fig. 2. ORTEPII (Johnson, 1976) drawing of a central molecule of (I) and the eight neighbors to which it is linked by C—H$\cdots$O interactions. Displacement ellipsoids are drawn for 50% probability for all non-H atoms; spheres of arbitrary small radii depict H atoms. C—H$\cdots$O interactions are depicted by dashed lines and are labeled a–d in the order of appearance in Table 2.

For structural comparisons of the anhydride portion of (I), the corresponding portions of phthalic anhydride (hereafter PA; Bates & Cutler, 1977) and 1,4,5,8-naphthalenetetracarboxylic 1,8:4,5-dianhydride (hereafter NTD; Blackburn et al., 1997) appear quite suitable. The mean values of the lengths of the three common pairs of chemically equivalent bonds in the anhydride groups of (I), PA and NTD are, respectively; 1.474 (2), 1.468 (3) and 1.478 (2)Å; 1.190 (2), 1.192 (4) and 1.186 (2) Å; and 1.398 (2), 1.394 (4) and 1.390 (2) Å. Thus, there is very good agreement for chemically equivalent bonds both within and among the anhydride groups of these three molecules. Somewhat surprisingly, (I) is more closely planar than PA or NTD, for which the maximum deviations from the best-fit planes are given as 0.04 and 0.045 (2) Å, respectively.

Selected bond distances and angles are given in Table 1. All distances and angles fall within normal ranges. The closest intermolecular approaches, excluding pairs of atoms involved in the tabulated C—H$\cdots$O interactions, are between C6 and C12(x, $\frac{1}{2} - y$, $-\frac{1}{2} + z$) and are 0.03 Å greater than the corresponding Bondi (1964) van der Waals radius sum.

Experimental

The title compound was obtained from Chemsyn Science Laboratories as a bright yellow, finely crystalline material.

Sublimed as received, it produced satisfactory single crystals. One such crystal, uncut, constituted the experimental sample.

Crystal data

$C_{12}H_{16}O_3$	Mo $K\alpha$ radiation
$M_r = 198.18$	$\lambda = 0.71073$ Å
Monoclinic	Cell parameters from 25
$P2_1/c$	reflections
$a = 7.714\,(2)$ Å	$\theta = 14.2–14.9°$
$b = 17.848\,(2)$ Å	$\mu = 0.11$ mm^{-1}
$c = 6.910\,(2)$ Å	$T = 296$ K
$\beta = 107.34\,(2)°$	Uncut column
$V = 908.0\,(4)$ Å^3	$0.46 \times 0.27 \times 0.15$ mm
$Z = 4$	Yellow
$D_x = 1.450$ Mg m^{-3}	
D_m not measured	

Data collection

AFC-5S diffractometer	$h = 0 \rightarrow 10$
ω scans	$k = -23 \rightarrow 23$
Absorption correction: none	$l = -8 \rightarrow 8$
2328 measured reflections	6 standard reflections
2083 independent reflections	every 150 reflections
1141 reflections with	intensity variation: $\pm 2.4\%$
$I > 2\sigma I$	(average maximum
$R_{int} = 0.013$	relative intensity)
$\theta_{max} = 27.49°$	

Refinement

Refinement on F^2	$(\Delta/\sigma)_{max} = 0.0002$
$R(F) = 0.045$	$\Delta\rho_{max} = 0.34$ e Å^{-3}
$wR(F^2) = 0.052$	$\Delta\rho_{min} = -0.32$ e Å^{-3}
$S = 1.62$	Extinction correction: none
2080 reflections	Scattering factors from
160 parameters	Stewart et al. (1965) for
All H-atom parameters	H and Creagh & McAuley
refined	(1992) for C, N and O
$w = 1/\sigma^2(F^2)$, where	
$\sigma^2 = \sigma_{cs}^2 + (0.003I)^2$	

Table 1. Selected geometric parameters (Å, °)

O1—C11	1.192 (2)	C1—C2	1.361 (2)
O2—C11	1.395 (2)	C1—C11	1.476 (2)
O2—C12	1.400 (2)	C2—C12	1.472 (2)
O3—C12	1.188 (2)		
C11—O2—C12	108.8 (1)	O2—C12—O3	120.9 (2)
O1—C11—O2	120.3 (2)	O2—C12—C2	107.5 (1)
O1—C11—C1	132.0 (2)	O3—C12—C2	131.7 (2)
O2—C11—C1	107.7 (1)		

Table 2. C—H···O interactions (Å, °)

D—H···A	D—H	H···A	D···A	D—H···A
C3—H3···O1^i	0.98 (1)	2.69 (2)	3.313 (2)	122 (1)
C4—H4···O1^{iii}	0.93 (1)	2.67 (2)	3.453 (2)	142 (1)
C5—H5···O3^{iii}	0.98 (1)	2.52 (2)	3.326 (2)	140 (1)
C7—H7···O2^{iv}	0.97 (2)	2.61 (2)	3.336 (2)	132 (1)

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

Table 3. First- and basic second-level graph-set descriptors involving C—H···O interactions designated a–d in order as given in Table 2

	a	b	c	d
a	$C(6)$	$C_2^2(5)$	$C_2^2(11)$	$C_2^2(12)$
b		$C(7)$	$R_4^2(20)$	$R_4^4(20)$
c			$C(8)$	$C_2^2(7)$
d				$C(7)$

Scan widths were $(1.40 + 0.35\tan\theta)°$ in ω, with a background/scan time-ratio of 0.5. The data were corrected for Lorentz and polarization effects. The Laue group assignment, systematic absences and centrosymmetric intensity statistics for the quadrant of data collected $(h,k,\pm l)$ indicated space group $P2_1/a$ (No. 14). Prior to refinement, the cell and data were transformed to the standard setting $P2_1/c$; since refinement proceeded well, it was adopted. Difference Fourier methods were used to locate initial H-atom positions, which were refined isotropically. In late stages of refinement, the predicted extinction coefficient was negative, and extinction was not included in the model. However, three large low-angle reflections (002, $1\bar{1}0$ and $11\bar{2}$) appeared to suffer from extinction and were not included in the final least-squares cycles. The maximum positive residual peak is located ~ 0.9 Å from C5 and C10; the maximum negative peak is located ~ 0.5 Å from C8.

Data collection: MSC/AFC Diffractometer Control Software (Molecular Structure Corporation, 1988). Cell refinement: MSC/AFC Diffractometer Control Software. Data reduction: TEXSAN (Molecular Structure Corporation, 1995). Program(s) used to solve structure: SHELXS86 (Sheldrick, 1985). Program(s) used to refine structure: TEXSAN. Molecular graphics: ORTEPII (Johnson, 1976). Software used to prepare material for publication: TEXSAN and PLATON (Spek, 1990).

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Ethylene bis(dimethyldithiocarbamate) and butane-1,4-diyl bis(dimethyldithiocarbamate)

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Abstract

In the crystals of the title compounds, $C_8H_{16}N_2S_4$, (I), and $C_{10}H_{20}N_2S_4$, (II), the molecules lie about inversion centres. In both structures, the C=S bonds in the two dithiocarbamate units are oriented *trans* to each other. In (I), the ethylene bridge and the bridged S atoms adopt a *trans* planar conformation and form a dihedral angle of 84.4 (2)° with the dimethyldithiocarbamate plane. The molecule of (II) is nearly planar; in the crystal, the molecules are arranged in sheets which are stacked, 3.874 (2) Å apart, parallel to (206) planes.

Comment

Since the discovery of alkylene dithiocarbamate $[R^1R^2NC(=S)SR^3SC(=S)NR^2R^1; R^1 = H, C_{1-18}; R^2 = C_{1-18}; R^3 = C_{1-10}$, divalent hydrocarbon] as a plant-protective fungicide, many of its derivatives have been synthesized (Yagihara *et al.*, 1975; Kubota *et al.*, 1977; Roethling *et al.*, 1983). It was recently discovered that various alkylene bis(dialkyldithiocarbamates) could be used as flotation agents in Au and Cu recovery (Di Biase & Bush, 1991) and as vulcanization accelerator agents in the curing of diene rubbers. This paper reports the structural details of two such derivatives.

In the crystals of both (I) and (II), the asymmetric unit contains one half of the molecule, the other half being inversion related. In both structures, each S_2CNMe_2 subunit has one C—S single bond [1.758 (3) in (I) and 1.778 (2) Å in (II)] and one C=S double bond [1.664 (3) in (I) and 1.675 (2) Å in (II)]. The S_2CNMe_2 units are bonded to the bridging ethylene and butylene by C—S single bonds. In both compounds, the two C=S bonds are oriented *trans* to each other. Shorter C—N bond distances in the S_2CN units [1.328 (4) in (I) and 1.328 (2) Å in (II)] are indicative of considerable double-bond character. All these bond distances (S—C, S=C and C—N) are comparable with the corresponding distances in the methylene bis(dialkyldithiocarbamate) structure (Sharma *et al.*, 1991; Gimeno *et al.*, 1996).
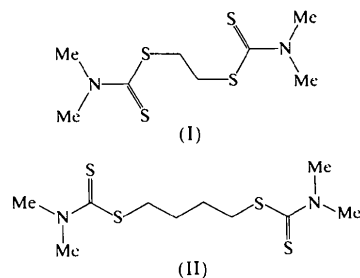
In (I), the dimethyldithiocarbamate group is planar to within 0.023 (3) Å and atoms S1, C4, C4^i and S1^i adopt a *trans* planar conformation; these two planes form a dihedral angle of 84.4 (2)°. The non-H atoms in (II) are nearly coplanar with maximum deviations of −0.071 (1) and 0.071 (1) Å for S1 and S1^i, respectively.

In both structures, the S2···C4 contact distances [3.101 (5) and 3.113 (2) Å] are significantly shorter than the sum of the van der Waals radii (3.55 Å) indicating the formation of an incipient bond between these atoms and the occurrence of ring-opening/ring-closing tautomerism (Schumaker *et al.*, 1991). Other significant intramolecular short contacts in these structures are S1···N1 [2.585 (4) and 2.607 (2) Å], S1···C2 [2.852 (4) and 2.858 (2) Å], S2···N1 [2.650 (4) and 2.660 (2) Å], S2···C1 [3.011 (5) and 3.019 (2) Å] and S1···C5 [2.710 (2) Å in (II)]. The shortest intermolecular contact in the two structures is S1···C4(1−x, −y, 1−z) [2.769 (4) Å], which is observed in (I). In the crystal of (II), the molecules form a zigzag arrangement in a plane, the molecular sheets being stacked parallel to (206) planes, 3.874 (2) Å apart.
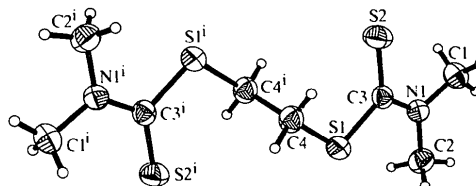

Fig. 1. The structure of (I) showing 50% probability displacement ellipsoids and the atom-numbering scheme.