Acta Cryst. (1985). C**41**, 1648–1650

Structure of 2-Anilino-*N,N'*-di-*tert*-butyl-2-(*N*-phenylsulfenamoyl)malonamide

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(*Received* 29 *April* 1985; *accepted* 19 *July* 1985)

Abstract. $C_{23}H_{32}N_4O_2S$, $M_r = 428{\cdot}6$, $P2_1/n$, $a = 13{\cdot}814\,(1)$, $b = 10{\cdot}354\,(1)$, $c = 16{\cdot}980\,(1)$ Å, $\beta = 96{\cdot}22\,(1)°$, $V = 2414{\cdot}4\,(3)$ Å^3, $D_x = 1{\cdot}179$ Mg m^{-3}, $Z = 4$, Cu $K\alpha$, $\lambda = 1{\cdot}54184$ Å, $\mu = 1{\cdot}35$ mm^{-1}, $F(000) = 920$, $T = 295\,(2)$ K, $R = 0{\cdot}051$ for 4416 unique reflections. An unexpected structure of the product $C_{23}H_{32}N_4O_2S$ furnished by the reaction of malonic acid dihydrochloride with sulfur diimide and aniline was revealed by X-ray analysis. The elongated S—C = 1·904 (3) Å single bond may be attributed to the high electrophilicity of the prochiral C atom at the centre of the title molecule. There is a short close contact [2·819 (2) Å] between S and O belonging to one of the carbonyl groups which is significantly shorter than the sum of the van der Waals radii (3·25 Å). This S···O close contact is strong enough to induce the shortening of the S—N single bond [1·656 (2) Å] in the *N*-phenylsulfenamoyl group accompanied by an N—S···O angle of 156·4 (1)°.

Introduction. The X-ray analysis of the title compound revealed a structure basically different from that which was suggested originally by Fischer & Boldt (1985): *N-tert*-butyl-*N*-(N^2-*tert*-butyl-N^2-phenylsulfinamidino)-*N'*-phenylmalonamide. The structure discussed below enabled us to shed light on the most probable reaction mechanism (Fischer, Boldt, Kálmán & Argay, 1985).

Experimental. Crystal dimensions: 0·45 × 0·55 × 0·80 mm. D_m not determined. Enraf–Nonius CAD-4 diffractometer. Graphite monochromator. Cell constants by least squares using 25 reflections with $47 \leq \theta \leq 50°$. Systematic absences $h0l$: $h + l = 2n + 1$, $0k0$: $k = 2n + 1$; $2\theta_{\max} = 150°$; h 0→17, k 0→12, l −21→21. Three standard reflections (7,0,$\overline{15}$, 1,10,2 and 686) showed 5·4% total loss of intensity during 73 h of exposure; correction for anisotropic decay performed with factors $\delta_{\max} = 1{\cdot}50$ and $\delta_{\min} = 0{\cdot}98$. Of 4785 measured unique reflections, 4416 with $F^2 \geq 5{\cdot}0\sigma(F^2)$ were taken as observed. Structure solved by *MULTAN*82 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982) using 297 $E \geq 1{\cdot}85$. Full-matrix least squares, $\sum w(\Delta F)^2$ minimized, 272 parameters refined. At $R = 0{\cdot}13$ an empirical absorption correction was performed with the program *DIFABS* (Walker & Stuart, 1983); min. and max. absorption corrections 0·80 and 1·29. Final $R = 0{\cdot}051$, $wR = 0{\cdot}054$, $R_{\rm tot} = 0{\cdot}055$, $S = 2{\cdot}78$, $w = [\sigma^2(F_o) + 0{\cdot}08F_o^2]^{-1}$. Max. and min. peak heights in final $\Delta\rho$ map ±0·21 e Å^{-3}. Extinction coefficient: 0·1997 ×10^{-5}. For non-H atoms $(\Delta/\sigma)_{\max} = 0{\cdot}56$. Positions of H atoms bound to C atoms were generated from assumed geometries; those belonging to N atoms were located in a difference Fourier synthesis at $R = 0{\cdot}064$; they were treated isotropically in the last three cycles of the refinement. Scattering factors from *International Tables for X-ray Crystallography* (1962). Programs applied: Enraf–Nonius *SDP* package with local modifications adapted to a PDP 11/34 minicomputer (64 K).

Discussion. A perspective view of the molecular structure computed from the final atomic coordinates listed in Table 1* is depicted in Fig. 1. The prochiral atom C(2) sits at the centre of a distorted tetrahedron, the smallest angle of which [104·5 (3)°] is formed by C(1)—C(2) and the long S(1)—C(2) bond, whilst the largest [115·0 (4)°] is found between the C(1)—C(2) and C(2)—N(3) bonds. The high electrophilicity of C(2) may account for the exceptionally long S(1)—C(2) bond (Table 2). It is even 0·066 (6) Å longer than the average of the three long S^{II}—C(sp^3) single bonds [1·838 (5) Å] observed in 6*H*,12*H*,18*H*-5,11,17-trithiatribenzo[*a,e,i*]cyclododecene (Párkányi, Kálmán & Nógrádi,

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and torsion angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42378 (36 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

0108-2701/85/111648-03$01.50

1975). In contrast with the elongated S(1)—C(2) bond the C(2)—N(3) bond is significantly shorter [1·430 (3) Å] than the 1·472 (5) Å regarded as the single-bond distance in the literature and assumed by the N(1)—C(8) and N(2)—C(4) single bonds [mean value: 1·473 (4) Å]. The structure exhibits two further types of C—N bonds. There are two $N(sp^2/sp^3)$—C_{ar} bonds with a mean distance of 1·409 (3) Å and two $N(sp^2/sp^3)$—$C(sp^2)$ bonds with a mean distance of 1·337 (3) Å. The N lone pairs delocalized towards the vicinal oxo groups account for the strong $N(sp^2/sp^3)$—$C(sp^2)$ bonds. The difference between the C(1)—C(2) and C(2)—C(3) single-bond lengths [$\Delta = 0{\cdot}028$ (4) Å] may be attributed to the formation of the S(1)···O(1) close contact [2·819 (2) Å] which is significantly shorter than the sum of the van der Waals radii of S and O (3·25 Å). This S···O close contact falls in the range reported by Kálmán, Koritsánszky, Kapovits & Kucsman (1982) for some *N*-carbonylsulfilimines.* The observed S···O distance would be even shorter (about 2·72 Å) if the C(1)—O(1) and C(2)—S(1) bonds – instead of being synclinal (Klyne & Prelog, 1960) – were nearly eclipsed (*i.e.* synperiplanar). However, the N(4)—S(1)···O(1) angle is far from 180° [156·4 (1)°] and the S···O no bond/single bond seems to influence the S(1)—N(4) bond since it is considerably shorter than the S^{II}—$N(sp^3)$ single bond (1·735 Å; Pauling, 1960). The observed molecular conformation is also influenced by intramolecular N—H···*A* and C_φ—H···*A* hydrogen bonds (Table 3). One intermolecular C_φ—H···O close contact may also be taken into account. In particular, contact No. 1 seems to weaken the S···O close contact, twisting the O(1)—C(1) bond about C(1)—C(2) by *ca* 30°. Owing to the open conformation of the bulky molecule no intermolecular hydrogen bond could be formed except for the above-mentioned weak contact No. 5.

Table 1. *Fractional coordinates and mean temperature factors for the non-hydrogen atoms, with e.s.d.'s in parentheses*

$B_{eq} = \frac{4}{3}$ trace (B**G**) where **G** is the direct metric tensor.

	x	y	z	B_{eq}(Å^2)
S(1)	0·04408 (5)	0·38091 (7)	0·86444 (4)	4·68 (2)
O(1)	0·1600 (1)	0·5645 (2)	0·7956 (1)	5·7 (1)
O(2)	−0·1550 (1)	0·5832 (1)	0·7908 (1)	4·7 (1)
N(1)	0·0847 (1)	0·5676 (2)	0·6699 (1)	4·6 (1)
N(2)	−0·0185 (1)	0·6913 (2)	0·8398 (1)	4·6 (1)
N(3)	−0·0617 (1)	0·4135 (2)	0·7159 (1)	4·2 (1)
N(4)	−0·0446 (1)	0·2738 (2)	0·8668 (1)	4·9 (1)
C(1)	0·0901 (1)	0·5412 (2)	0·7474 (1)	4·1 (1)
C(2)	−0·0015 (1)	0·4836 (2)	0·7750 (1)	3·8 (1)
C(3)	−0·0662 (1)	0·5922 (2)	0·8033 (1)	3·8 (1)
C(4)	−0·0626 (2)	0·8102 (2)	0·8680 (1)	4·6 (1)
C(5)	−0·1258 (2)	0·8722 (3)	0·7994 (2)	6·6 (1)
C(6)	0·0213 (2)	0·8993 (3)	0·8954 (2)	7·2 (1)
C(7)	−0·1202 (2)	0·7794 (3)	0·9361 (1)	5·9 (1)
C(8)	0·1591 (2)	0·6320 (3)	0·6281 (1)	6·1 (1)
C(9)	0·1805 (2)	0·7648 (3)	0·6649 (3)	9·8 (2)
C(10)	0·1164 (3)	0·6448 (6)	0·5431 (2)	12·1 (2)
C(11)	0·2509 (2)	0·5527 (4)	0·6343 (2)	7·5 (1)
C(12)	−0·0382 (1)	0·2905 (2)	0·6873 (1)	4·0 (1)
C(13)	−0·1146 (2)	0·2126 (3)	0·6566 (1)	5·3 (1)
C(14)	−0·0966 (2)	0·0942 (3)	0·6241 (2)	6·7 (1)
C(15)	−0·0037 (2)	0·0508 (3)	0·6221 (2)	6·7 (1)
C(16)	0·0726 (2)	0·1254 (3)	0·6543 (1)	5·8 (1)
C(17)	0·0564 (2)	0·2458 (2)	0·6866 (1)	4·8 (1)
C(18)	−0·1309 (2)	0·2893 (2)	0·9027 (1)	4·3 (1)
C(19)	−0·2100 (2)	0·2135 (3)	0·8775 (1)	5·5 (1)
C(20)	−0·2929 (2)	0·2184 (3)	0·9154 (2)	6·5 (1)
C(21)	−0·2987 (2)	0·2986 (3)	0·9788 (2)	6·4 (1)
C(22)	−0·2204 (2)	0·3770 (3)	1·0026 (1)	5·7 (1)
C(23)	−0·1376 (2)	0·3733 (2)	0·9655 (1)	4·9 (1)

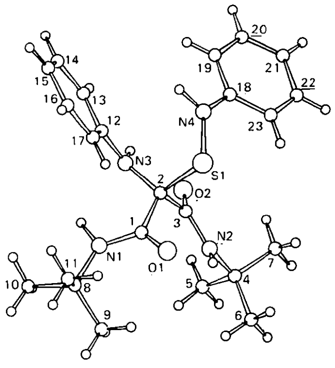

Fig. 1. Perspective view of the molecular geometry with atomic numbering. The numbers are for C atoms unless indicated otherwise. The H atoms are shown but not labelled.

Table 2. *Bond lengths* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

S(1)—N(4)	1·656 (2)	N(4)—C(18)	1·405 (3)	C(12)—C(17)	1·388 (4)
S(1)—C(2)	1·904 (3)	C(1)—C(2)	1·518 (3)	C(13)—C(14)	1·377 (5)
O(1)—C(1)	1·220 (3)	C(2)—C(3)	1·546 (3)	C(14)—C(15)	1·364 (5)
O(2)—C(3)	1·225 (3)	C(4)—C(5)	1·521 (4)	C(15)—C(16)	1·372 (5)
N(1)—C(1)	1·339 (3)	C(4)—C(6)	1·514 (5)	C(16)—C(17)	1·390 (4)
N(1)—C(8)	1·470 (4)	C(4)—C(7)	1·508 (4)	C(18)—C(19)	1·376 (4)
N(2)—C(3)	1·335 (3)	C(8)—C(9)	1·526 (6)	C(18)—C(23)	1·387 (4)
N(2)—C(4)	1·476 (4)	C(8)—C(10)	1·504 (5)	C(19)—C(20)	1·374 (5)
N(3)—C(2)	1·430 (3)	C(8)—C(11)	1·505 (5)	C(20)—C(21)	1·370 (5)
N(3)—C(12)	1·413 (3)	C(12)—C(13)	1·384 (4)	C(21)—C(22)	1·377 (5)
				C(22)—C(23)	1·365 (4)

N(4)—S(1)—C(2)	102·2 (2)	C(6)—C(4)—C(7)	110·1 (4)
C(1)—N(1)—C(8)	126·9 (4)	N(1)—C(8)—C(9)	109·0 (5)
C(3)—N(2)—C(4)	126·2 (4)	N(1)—C(8)—C(10)	106·4 (5)
C(2)—N(3)—C(12)	124·2 (4)	N(1)—C(8)—C(11)	110·3 (5)
S(1)—N(4)—C(18)	126·8 (3)	C(9)—C(8)—C(10)	110·6 (6)
O(1)—C(1)—N(1)	125·0 (4)	C(9)—C(8)—C(11)	109·8 (5)
O(1)—C(1)—C(2)	119·8 (4)	C(10)—C(8)—C(11)	110·8 (5)
N(1)—C(1)—C(2)	115·1 (4)	N(3)—C(12)—C(13)	117·5 (4)
S(1)—C(2)—N(3)	113·2 (3)	N(3)—C(12)—C(17)	123·7 (4)
S(1)—C(2)—C(1)	104·5 (3)	C(13)—C(12)—C(17)	118·8 (4)
S(1)—C(2)—C(3)	108·1 (3)	C(12)—C(13)—C(14)	120·4 (5)
N(3)—C(2)—C(1)	115·0 (4)	C(13)—C(14)—C(15)	120·9 (5)
N(3)—C(2)—C(3)	106·0 (3)	C(14)—C(15)—C(16)	119·3 (6)
C(1)—C(2)—C(3)	109·8 (3)	C(15)—C(16)—C(17)	120·8 (5)
O(2)—C(3)—N(2)	125·0 (4)	C(12)—C(17)—C(16)	119·7 (5)
O(2)—C(3)—C(2)	119·5 (4)	N(4)—C(18)—C(19)	118·8 (4)
N(2)—C(3)—C(2)	115·5 (4)	N(4)—C(18)—C(23)	122·4 (4)
N(2)—C(4)—C(5)	109·0 (4)	C(19)—C(18)—C(23)	118·7 (4)
N(2)—C(4)—C(6)	106·2 (4)	C(18)—C(19)—C(20)	120·5 (5)
N(2)—C(4)—C(7)	110·1 (4)	C(19)—C(20)—C(21)	120·9 (6)
C(5)—C(4)—C(6)	109·6 (4)	C(20)—C(21)—C(22)	118·5 (6)
C(5)—C(4)—C(7)	111·7 (4)	C(21)—C(22)—C(23)	121·2 (5)
		C(18)—C(23)—C(22)	120·1 (5)

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* A computer retrieval of S···O close contacts shorter than 3·25 Å from the Cambridge Crystallographic Data Files (July 1983) carried out by one of us (GyA) revealed 130 structures having such an S···O contact closing a four-membered hetero ring.

Table 3. *Relevant hydrogen bonds*

No.	*D*–H···*A*	*D*···*A* (Å)	H···*A* (Å)	*D*H···*A* (°)
1	N(2)–H···O(1^i)	2·961 (2)	2·23 (3)	139 (2)
2	N(1)–H···N(3^i)	2·754 (2)	2·27 (3)	118 (2)
3	N(3)–H···O(2^i)	2·593 (2)	2·09 (2)	113 (2)
4	C(17)–H···N(1^i)	3·370 (3)	2·85 (2)	117 (2)
5	C(22)–H···O(1^{ii})	3·491 (2)	2·77 (2)	137 (2)

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

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Acta Cryst. (1985). C**41**, 1650–1653

rel-(3*R*,3a*R*,8*S*,8a*R*)-3a-Hydroxy-1-oxo-6-daucen-8-yl *p*-Anisate (1) and *rel*-(1*S*,3*R*,3a*S*,4*S*,8*S*,8a*R*)-1,8-Diacetoxy-3-hydroxy-6-daucen-4-yl *p*-Anisate (2)*

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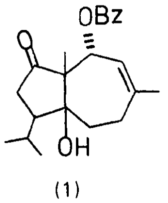
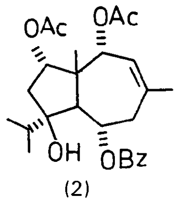
(*Received* 15 *May* 1985; *accepted* 16 *July* 1985)

Abstract. (1), $C_{23}H_{30}O_5$, $M_r = 386·49$, orthorhombic, $P2_12_12_1$, $a = 11·723$ (6), $b = 17·261$ (8), $c = 10·515$ (3) Å, $V = 2128$ (2) Å^3, $Z = 4$, $D_x = 1·206$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0·71069$ Å, $\mu = 0·90$ cm^{-1}, $F(000) = 832$, $T = 295$ K, $R = 0·044$ for 1448 independent reflections (θ:2θ scan). (2), $C_{27}H_{36}O_8$, $M_r = 488·59$, orthorhombic, $P2_12_12_1$, $a = 11·733$ (3), $b = 26·654$ (9), $c = 8·644$ (4) Å, $V = 2703$ (2) Å^3, $Z = 4$, $D_x = 1·200$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0·71069$ Å, $\mu = 0·94$ cm^{-1}, $F(000) = 1048$, $T = 295$ K, $R = 0·052$ for 1927 independent reflections (θ:2θ scan). The carotane-class sesquiterpenes were isolated from *Ferula communis* (Compositae). The five- and seven-membered rings are *cis* fused in compound (1) but *trans* fused in (2), which leads to conformational differences in the two compounds. The five-membered rings in both compounds exhibit envelope conformations with C(4) the flap in (1) and C(1) the flap in (2). The seven-membered ring in (2) is in an almost perfect chair conformation while that in (1) exhibits a distorted twist-chair conformation.

Introduction. *Ferula communis* L. subsp. *Communis* has been known as a medicinal since ancient times (Gunther, 1959) and has been used as an antihysteric and for the treatment of dysentery (French, 1971). *Ferula communis* was collected near Istanbul, Turkey, and the dried powdered roots were extracted with benzene. Chromatography led to the isolation of fourteen daucene-type sesquiterpene esters (Miski & Mabry, 1985). Because of the difficulty in determining relative stereochemistry and ester substitution patterns, the structures of two sesquiterpenes were determined by X-ray diffraction techniques. The absolute configuration can be assigned by comparison with known structures (Miski & Mabry, 1985).



(1)



(2)

Experimental. Syntex $P2_1$ diffractometer, θ:2θ scan, variable scan rate, $2\theta_{max} = 50°$, graphite-monochromated Mo $K\alpha$ radiation; lattice parameters from

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* IUPAC names: (1) *rel*-(3*R*,3a*R*,8*S*,8a*R*)-3a-hydroxy-3-isopropyl-6,8a-dimethyl-1-oxo-1,2,3,3a,4,5,8,8a-octahydro-8-azulenyl *p*-anisate; (2) *rel*-(1*S*,3*R*,3a*S*,4*S*,8*S*,8a*R*)-1,8-diacetoxy-3-hydroxy-3-isopropyl-6,8a-dimethyl-1,2,3,3a,4,5,8,8a-octahydro-4-azulenyl *p*-anisate.

0108-2701/85/111650-04$01.50