The bond lengths and the bond angles of the molecules are listed in Table 3. The average bond lengths in the O=C—C=C—OH moiety from O(2) to O(1) are 1.26, 1.43, 1.36 and 1.33 Å for *A*, *B*, *C* and *D*, respectively. They are similar to those observed in dimedone and MCPD. The structure of the naphthalene moiety does not differ significantly from that of naphthalene.

The dipole moments of the *A–B* and *C–D* chains, which originate in the O=C—C=C—OH moieties, are directed towards the same direction along the *a* axis, resulting in the polarity of the crystal. The situation is similar to the case of phenylmalonaldehyde (Semmingsen, 1977). Thus the crystal may show ferroelectric properties. However, a dielectric response of the crystal was not observed in the temperature range 300–450 K under 10 kHz modulation. Neither dynamic processes nor phase transitions were observed in the solid-state ^{13}C NMR (CP/MAS) measurement even when the temperature was raised to 393 K. Therefore, it was concluded that the hydroxyl protons are tightly fixed at a particular site of the hydrogen bond even at high temperatures.

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Structure of 5-(1-Methyl-2,1-benzisothiazol-3-ylideneamino)-2,4-pentadienal

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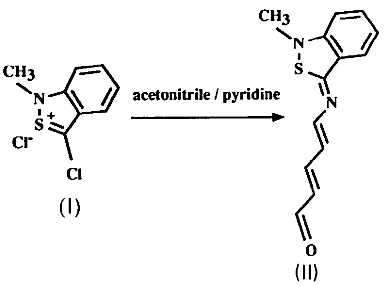
Abstract. $C_{13}H_{12}N_2OS$, $M_r = 244.31$, monoclinic, $P2_1/a$, $a = 7.743$ (2), $b = 12.430$ (5), $c = 12.776$ (5) Å, $\beta = 90.52$ (3)°, $V = 1229.6$ (7) Å^3, $Z = 4$, $D_x = 1.32$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, graphite monochromator, $\mu = 0.236$ mm^{-1}, $F(000) = 512$, $T = 295$ K, $R = 0.040$, $wR = 0.049$ for 2958 independent reflections collected. This is only the third example of a crystal structure containing a 2,1-benzisothiazole ring system. Bond lengths in the isothiazole ring of the title compound suggest much less double-bond character than observed in the other two known structures. The molecule is essentially planar and packs in the crystal with the benzisothiazole rings stacked in the [100] direction.

Introduction. As part of ongoing studies of benzisothiazoles, an attempt was made to form a 2,1-benzisothiazol-3-ylideneacetonitrile by treating 3-chloro-1-methyl-2,1-benzisothiazolium chloride (I) with acetonitrile in pyridine. Instead, the title compound (II) was afforded on work up.



Experimental. 3-Chloro-1-methyl-2,1-benzisothiazolium chloride (0.220 g, 1.0 mmol) in acetonitrile (10 mL) and pyridine (2 mL) was boiled for 15 min.

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Dilution with water gave a deep-red solution which was extracted with chloroform. Evaporation gave a deep-red oil which was chromatographed on silica gel using chloroform as an eluent. The red band was isolated and gave a dark-red oil which crystallized from ethanol as intensely coloured red prisms with m.p. 393 K. A Rigaku AFC-6S diffractometer was employed for data collection on a crystal measuring 0.3 × 0.3 × 0.3 mm. An ω–2θ scan mode was used with data being collected in the range $0 < 2\theta < 55°$, h 0→10, k 0→16, l − 17→17. Post-collection analysis revealed poor scattering beyond $2\theta = 45°$. Final cell parameters were obtained from the setting angles of 23 reflections in the range $23 < 2\theta < 34°$. Lorentz and polarization corrections were applied, but no absorption correction was warranted. Overall, 1579 of the 2958 independent reflections (or 53%) were considered observed with $I \geq 3\sigma(I)$. Three reflections which were periodically monitored for intensity and orientation control showed no significant deviation over the period of the experiment. The total number of reflections measured (less standards) was 3174 including 140 systematically absent reflections; 76 reflections were merged with $R_{\rm int} = 0.015$.

The structure was solved by direct methods and refined using programs in the *TEXSAN** software package. The structure was refined on F, initially with non-H atoms only. H-atom positions were subsequently determined from difference Fourier maps and included for the remaining cycles of refinement. Convergence for 202 variables was reached at $R = 0.040$ and $wR = 0.049$ using observed data only; for all data $R = 0.114$ and $wR = 0.057$. The function minimized throughout refinement was $\sum w\Delta^2$ ($\Delta = |F_o| - |F_c|$), where $w = \sigma^{-2}(F_o)$; $S = 1.644$ and maximum $\Delta/\sigma = 0.19$ on the final cycle. The final difference Fourier map showed random fluctuations of ± 0.2 e Å^{-3}. Scattering factors for all non-H atoms were from Cromer & Waber (1974) and from Stewart, Davidson & Simpson (1965) for H atoms.† Final atomic positional parameters and equivalent isotropic thermal parameters are given in Table 1.

Table 1. *Final fractional positional parameters and equivalent isotropic thermal parameters* (Å^2) *with e.s.d.'s in parentheses*

$$B_{\rm eq} = (8\pi^2/3)\sum_{i=1}^{3}\sum_{j=1}^{2} U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$B_{\rm eq}$
S	0.03048 (9)	0.23465 (5)	0.70369 (5)	4.68 (3)
O	0.2276 (3)	−0.4142 (2)	0.5054 (2)	8.6 (1)
N(1)	−0.0298 (3)	0.3471 (2)	0.7675 (2)	5.2 (1)
N(2)	−0.0306 (2)	0.0455 (2)	0.8068 (1)	4.06 (9)
C(1)	−0.0923 (3)	0.3263 (2)	0.8652 (2)	4.0 (1)
C(2)	−0.0992 (3)	0.2169 (2)	0.8888 (2)	3.7 (1)
C(3)	−0.1617 (3)	0.1826 (2)	0.9848 (2)	4.4 (1)
C(4)	−0.2188 (3)	0.2577 (2)	1.0549 (2)	5.1 (1)
C(5)	−0.2123 (4)	0.3666 (3)	1.0306 (2)	5.2 (1)
C(6)	−0.1477 (3)	0.4022 (2)	0.9372 (2)	4.9 (1)
C(7)	−0.0354 (3)	0.1500 (2)	0.8056 (2)	3.7 (1)
C(8)	0.0393 (3)	−0.0067 (2)	0.7232 (2)	4.2 (1)
C(9)	0.0483 (3)	−0.1142 (2)	0.7162 (2)	4.3 (1)
C(10)	0.1241 (3)	−0.1686 (2)	0.6302 (2)	4.3 (1)
C(11)	0.1366 (4)	−0.2746 (2)	0.6171 (2)	5.0 (1)
C(12)	0.2141 (4)	−0.3201 (3)	0.5266 (2)	6.0 (2)
C(13)	0.0206 (4)	0.4513 (3)	0.7271 (3)	5.5 (2)

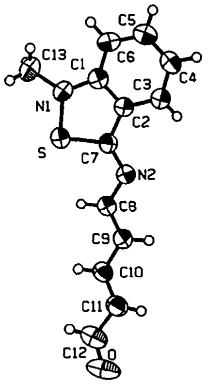

Fig. 1. *ORTEP*II plot (Johnson, 1976) of the title compound with thermal ellipsoids displayed at the 50% probability level.

Discussion. A plausible mechanism for the reaction involves quaternization of the pyridine N atom by the reactive carbon, C(7), of the benzisothiazole (labelling given in Fig. 1), followed by nucleophilic attack of water on the pyridinium 2-position, and ring opening. 3-Chloro-2,1-benzisothiazoles and 1,2-benzisothiazolium salts are known to be attacked at C(7) by nucleophiles (Davis, 1985), and pyridinium salts give ring-opened products in base (Scriven, 1984). The reaction is related to the product of a pyridine caffeine coupling reaction (Kigasawa, Ohkubo, Kohagisawa, Shimizu, Saitoh & Kametani, 1976).

A search of the Cambridge Structural Database revealed only two crystal structures of compounds containing the 2,1-benzisothiazole moiety, *viz.* 5-chloro-2,1-benzisothiazole (CBIT) (Davis, Mackay & Denne, 1972) and 2,4,4-trichloro-1,4-dihydronaphth[1,8-*cd*]isothiazole-1,1-dioxide (TCNS) (Brummer & Weiss, 1987). The isothiazole ring in (II) has much less double-bond character than observed in the CBIT and TCNS structures. In CBIT

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* An integrated system of crystal structure solution, refinement and analysis programs available from Molecular Structure Corporation (1985). The package contains versions of *MITHRIL* (Gilmore, 1984), *ORFLS* (Busing, Martin & Levy, 1962) and *ORFFE* (Busing, Martin & Levy, 1964).

† Lists of refined H-atom positional and isotropic thermal parameters, anisotropic thermal parameters, bond distances and angles involving H atoms, torsion angles, least-squares planes, and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54645 (29 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: BR0004]

Table 2. *Bond lengths* (Å) *and angles* (°) *with e.s.d.'s in parentheses for present structure* (II), *CBIT* (*Davis, Mackay & Denne*, 1972) *and TCNS* (*Brummer & Weiss*, 1987)

	(II)	CBIT	TCNS
C(1)—C(2)	1.393 (3)	1.419 (7)	1.460 (3)
C(2)—C(7)	1.441 (3)	1.378 (7)	1.377 (3)
C(7)—S	1.754 (2)	1.664 (5)	1.776 (3)
S—N(1)	1.686 (2)	1.636 (5)	1.690 (3)
N(1)—C(1)	1.368 (3)	1.359 (7)	1.294 (3)
C(2)—C(3)	1.390 (3)	1.413 (7)	1.369 (3)
C(3)—C(4)	1.370 (3)	1.341 (7)	1.503 (3)
C(4)—C(5)	1.389 (3)	1.410 (7)	1.504 (3)
C(5)—C(6)	1.371 (4)	1.348 (7)	1.329 (3)
C(6)—C(1)	1.389 (3)	1.422 (7)	1.446 (3)
C(7)—N(2)	1.300 (3)		
N(2)—C(8)	1.365 (3)		
C(8)—C(9)	1.341 (4)		
C(9)—C(10)	1.421 (3)		
C(10)—C(11)	1.332 (4)		
C(11)—C(12)	1.425 (4)		
C(12)—O	1.205 (4)		
C(1)—C(2)—C(7)	112.9 (2)	109.5 (3)	111.9 (2)
C(2)—C(7)—S	107.8 (2)	109.4 (3)	105.7 (2)
C(7)—S—N(1)	93.2 (1)	97.7 (3)	96.2 (1)
S—N(1)—C(1)	112.7 (2)	107.1 (3)	108.3 (2)
N(1)—C(1)—C(2)	119.5 (2)	116.3 (3)	117.8 (2)
C(1)—C(2)—C(3)	120.4 (2)	120.3 (3)	125.4 (2)
C(2)—C(3)—C(4)	119.0 (3)	117.3 (3)	117.6 (2)
C(3)—C(4)—C(5)	120.4 (3)	122.8 (3)	115.7 (2)
C(4)—C(5)—C(6)	121.5 (3)	121.0 (3)	123.6 (2)
C(5)—C(6)—C(1)	118.3 (3)	119.1 (3)	121.4 (2)
C(6)—C(1)—C(2)	120.4 (2)	119.5 (3)	116.3 (2)
C(6)—C(1)—N(1)	126.1 (2)	124.2 (3)	125.9 (2)
C(7)—C(2)—C(3)	126.7 (2)	130.2 (3)	122.7 (2)
S—N(1)—C(13)	119.5 (2)		
C(1)—N(1)—C(13)	126.4 (2)		
C(2)—C(7)—N(2)	125.4 (2)		
S—C(7)—N(2)	126.8 (2)		
C(7)—N(2)—C(8)	118.5 (2)		
N(2)—C(8)—C(9)	123.1 (2)		
C(8)—C(9)—C(10)	123.2 (2)		
C(9)—C(10)—C(11)	126.8 (3)		
C(10)—C(11)—C(12)	121.8 (3)		
C(11)—C(12)—O	127.3 (4)		

the S—C distance is 1.664 (7) Å (Table 2), whereas a value of 1.776 (3) Å is observed in TCNS. These lengths are consistent with considerable double-bond character in the former compound and mostly single-bond character in the latter. In the present structure the S—C bond is closer in length to that in TCNS, with a value of 1.754 (2) Å, and may, therefore, be best described as single. In CBIT, where three resonance forms contribute to the average structure, the observed S—N distance is 1.636 (7) Å. The corresponding bonds in TCNS and in the title compound are 1.690 (2) and 1.686 (2) Å, respectively, indicating the decreased double-bond character between S and N compared with CBIT. Similar comparisons can be made for the other bonds in the ring.

The changes in bonding in the isothiazole ring are also reflected in the geometry of the attached aromatic ring. As in CBIT, the present structure shows aromatic C—C bond lengths which are symmetrical about the line extending between the midpoints of C(1)—C(2) and C(4)—C(5). However, the bond lengths are significantly different from the corresponding bonds in CBIT. While the present structure lacks the substitution of CBIT, the effect of the monochloro substituent alone in that molecule is insufficient to account for the distortion in its aromatic ring (Domenicano, Vaciago & Coulson, 1975). Therefore, an effect due to the electronic environment presented by the adjacent isothiazole ring is inferred. The aromatic C—C bond lengths in (II) are much less varied than those in CBIT owing to the two resonance forms maintaining the equivalent of three double bonds in the present structure compared to two of the three resonance forms of CBIT in which the aromatic ring contains only two double bonds. The TCNS molecule, containing a saturated C atom at C(3) (in the present labelling scheme) is not a candidate for legitimate comparison of these bonds.

The C(7)—N(2) bond has a length of 1.300 (3) Å which places it mid-range of imino bond distances observed in similar structures where the C atom is part of a five-membered ring; *e.g.*, the related thiadiazolo and dithiadiazolo compounds display imino bond lengths in the range 1.24–1.32 Å (Sato, Kinoshita, Hata & Tamura, 1977, 1980; Leban, 1976; Gieren & Dederer, 1978). Constraints imposed by the isothiazole ring in (II) yield bond angles of 107.8 (2), 125.4 (2) and 126.8 (2)° about C(7) (Table 2). Despite these non-ideal bond angles, the hybridization of C(7) is considered sp^2. The unconstrained bond angle of 118.3 (3)° for C(7)—N(2)—C(8) indicates that N(2) is also sp^2 hybridized. Burke-Laing & Laing (1976) have correlated C(sp^2)—N(sp^2) bond lengths with bond order and based on their data it appears that the C(7)—N(2) bond, of length 1.300 (3) Å in the present structure, does not exhibit complete double-bond character, but has a bond order closer to 1.75. This lower bond order is consistent with the expected delocalization of electrons into the conjugated chain.

The remainder of the chain, *viz.* the pentadienal fragment, manifests a geometry which is identical, within experimental error, to the same fragment in *N*,*O*-diacetyl-5-*p*-chloroanilino-4-hydroxypenta-2,4-dienal (Denne & Mackay, 1974). C—C and C=C bond lengths increase slightly in the direction of the non-bonded chain terminus. This same trend is

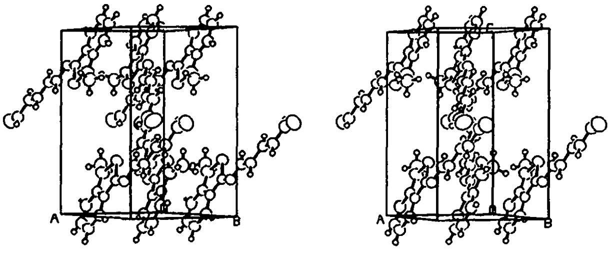

Fig. 2. *PLUTO* stereo plot (Motherwell & Clegg, 1978) of the unit-cell contents viewed approximately down the [110] direction.

observed in similar conjugated alkyl systems (Denne & Mackay, 1974; Wong, 1978).

The molecule, (II), is essentially planar with an average deviation of 0.03 Å and with C(13) deviating 0.172 Å away from the least-squares plane (Hamilton, 1964) through all non-H atoms. Molecules are packed with the molecular plane parallel to the (202) plane (Fig. 2). The benzisothiazole ring (x, y, z) overlaps an adjacent ring ($x - \frac{1}{2}$, $\frac{1}{2} - y$, z) resulting in a π-stacked column of rings in the [100] direction.

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Structure of 3-(2,4-Dimethyl-6-methylsulfonyloxyphenyl)-3-methylbutyric Acid

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Abstract. $C_{14}H_{20}O_5S$, $M_r = 300.38$, monoclinic, $P2_1/c$, $a = 10.5276\,(7)$, $b = 10.417\,(2)$, $c = 28.385\,(3)$ Å, $\beta = 104.583\,(9)°$, $V = 3012.0\,(3)$ Å^3, $Z = 8$, $D_x = 1.33$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 1.54178$ Å, $\mu = 18.6$ cm^{-1}, $F(000) = 1280$, $T = 292$ K, final $R = 0.046$ for 2977 observed reflections. Two symmetry-independent molecules, which have similar conformations, are interconnected by a pair of hydrogen bonds between their hydroxyl groups to form a dimer. In both molecules short intramolecular contacts between atoms of the side chains are observed. The deformations of the phenyl ring are similar to those previously observed in analogous structures and can be attributed to steric effects of the methyl substituents.

Introduction. This X-ray determination of the structure of 3-(2,4-dimethyl-6-methylsulfonyloxyphenyl)-3-methylbutyric acid (I) continues our studies on the influence of substituents and their intermolecular interactions on conformational restrictions in molecules. Milstein & Cohen (1972) and Borchardt & Cohen (1972*a*,*b*) described the influence of substituents, the methyl groups located mainly at C(3) and C(2′)* (see Fig. 1), on the rate of lactonization of *o*-hydroxyhydrocinnamic acid and its derivatives. They found that the rate of this reaction could be

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* The atom labelling of the title compound (see Fig. 1) has been adopted, for the sake of clarity, for all other structures discussed in this paper.