Studies on Heterocyclic Compounds. Part XVI.[1] Crystal and Molecular Structures of Three Products of 1,4-Dipolar Cycloaddition of Dimethyl Acetylenedicarboxylate to Benzothiazole

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Benzothiazole reacts with dimethyl acetylenedicarboxylate in methanol to give tetramethyl 1*H*-pyrido[2,1-*b*]-benzothiazole-1,2,3,4-tetracarboxylate (6) and dimethyl 4-formyl-2,3-dihydro-1,4-benzothiazine-2,3-dicarboxylate (7). A similar reaction of benzothiazole with dimethyl acetylenedicarboxylate in dimethylformamide affords tetramethyl 4a*H*-pyrido[2,1-*b*]benzothiazole-2,3,4,4a-tetracarboxylate (8). The structures of these compounds were confirmed by the ^{1}H and ^{13}C n.m.r. and mass spectra and *X*-ray analyses.

REID *et al.*[2,3] in 1964 reported a reaction between thiazole and dimethyl acetylenedicarboxylate in methanol which gave trimethyl pyrrolo[2,1-*b*]thiazole-5,6,7-tricarboxylate (1). From these reagents in dimethylformamide, however, they obtained a compound which they considered could possess either a [5.2.0] bicyclic structure (2) or a nine-membered ring structure (3), on the basis of n.m.r. spectra.

Acheson *et al.*[4] later reported that the reaction of dimethyl acetylenedicarboxylate with thiazoles, benzothiazole, and benzoxazole gave 2 : 1 adducts. In the case of benzothiazole, with methanol as solvent, a compound considered to be tetramethyl 4a*H*-pyrido[2,1-*b*]-benzothiazole-1,2,3,4-tetracarboxylate (6′) was obtained in fair yield (21%) at 0 °C.[4] Reid *et al.*[3] reported that trimethyl pyrrolo[2,1-*b*]benzothiazole-1,2,3-tricarboxylate (7′), m.p. 135—136°, was obtained from the reaction of benzothiazole with dimethyl acetylenedicarboxylate in methanol, but gave no analytical or spectral data.

We now describe a re-examination of the products from benzothiazole and dimethyl acetylenedicarboxylate by means of ^{1}H and ^{13}C n.m.r. and mass spectroscopy and *X*-ray analysis.

We have already reported briefly [1] the isolation of the abnormal addition product, dimethyl 4-formyl-2,3-dihydro-1,4-benzothiazine-*trans*-2,3-dicarboxylate (7), from benzothiazole and dimethyl acetylenedicarboxylate in methanol, and the confirmation of its structure by *X*-ray analysis. Treatment of benzothiazole with 2 mol. equiv. of dimethyl acetylenedicarboxylate in methanol at room temperature afforded 5% of tetramethyl 1*H*-pyrido[2,1-*b*]benzothiazole-1,2,3,4-tetracarboxylate (6) as yellow prisms, m.p. 239—240°, and 8% of the adduct (7) [1] as colourless prisms, m.p. 135—136°. The former product (6) was recently obtained by the same reaction by Acheson *et al.*[5] Its mass spectrum showed a parent peak at *m/e* 419, and high resolution measurements showed an initial loss of CH_3O. The i.r. spectrum of (6) showed absorptions at 1 736, 1 712, and 1 659 cm^{-1} (ester). The ^{1}H n.m.r. and ^{13}C n.m.r. (Table 1) spectra were in full agreement with structure (6), which was finally proved by an *X*-ray analysis.

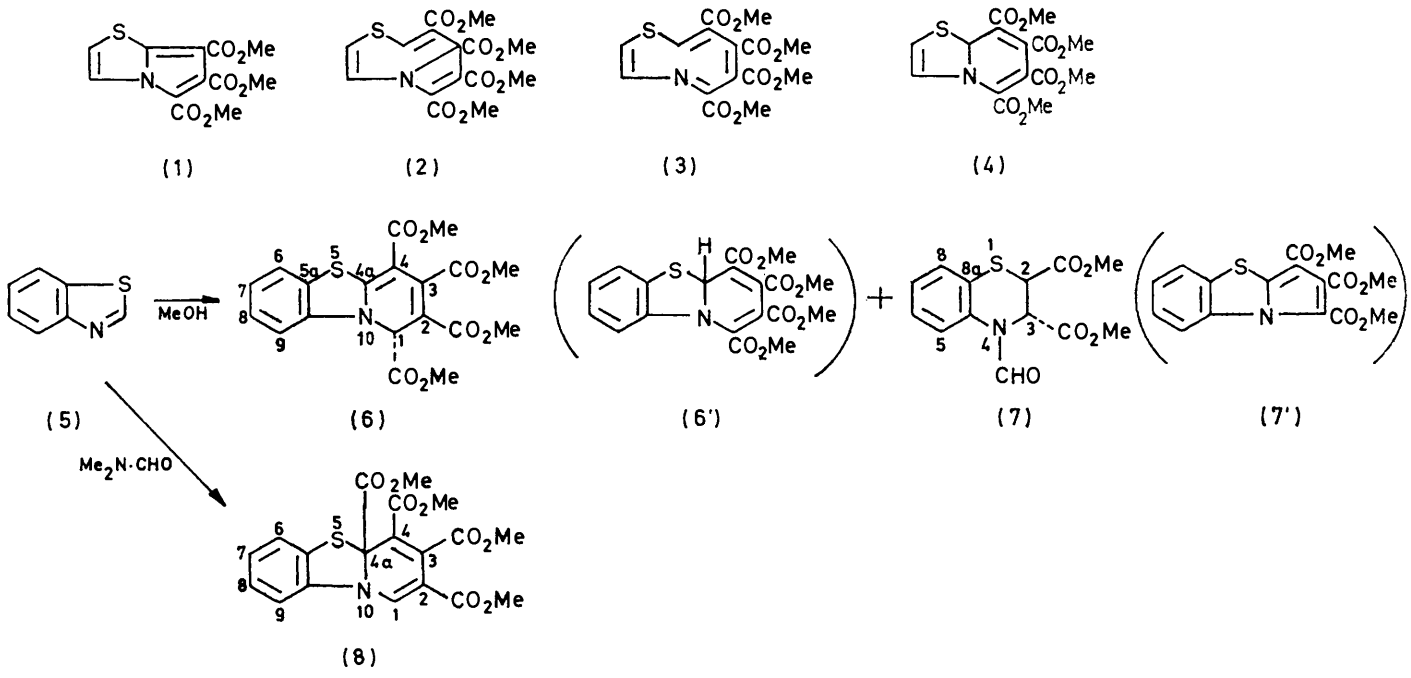
The crystals of (6) are triclinic ($a = 10.13_9$, $b = 10.22_4$, $c = 11.23_9$ Å, $\alpha = 71.8_5°$, $\beta = 109.5_2°$, $\gamma = 119.5_1°$, space group $P\bar{1}$) and there are two molecules in the unit cell. Intensity data were collected with a Philips four-circle automatic diffractometer by using monochromated Cu-K_α radiation (λ 1.5418 Å). A total of 1 550 independent structure factors out of the 2 662 theoretically possible were obtained. The structure was solved by the heavy-atom (sulphur) method and was refined by the block-diagonal-matrix least-squares method to a final *R* value of 0.074. Bond lengths and angles are given in Table 2.

Compound (7) is probably the substance obtained by Reid *et al.*[3] but formulated as (7′); it showed M^+ 295 and an initial loss of CO in the mass spectrum; details and high resolution data are available in the Supplementary Publication. The i.r. and ^{1}H n.m.r. spectra show the expected features including a low-field formyl proton n.m.r. signal. The ^{13}C n.m.r. spectrum (Table 1) shows the bridgehead carbon atom signals (=C–S and =C–N) at 122.3 and 133.7 p.p.m., respectively; the CHO and two CO_2Me signals appear at 161.4, 167.5, and 169.0 p.p.m., respectively (*cf.*[6] HCO·NMe$_2$ signal at 162.4 p.p.m.). Bond lengths and angles obtained in the *X*-ray analysis [1] are given in Table 3.

A similar reaction of benzothiazole with 2 mol. equiv. of dimethyl acetylenedicarboxylate in dimethylformamide solution at room temperature afforded tetramethyl 4a*H*-pyrido[2,1-*b*]benzothiazole-2,3,4,4a-tetracarboxylate (8) in 10% yield. Compound (8) is identical (m.p., mixed m.p., and u.v. and n.m.r. spectra) with the compound originally described [4] as (6′), but now considered [5] to have structure (8) in agreement with our

[1] Part XV, H. Ogura and H. Takahashi, *J. Org. Chem.*, 1974, **39**, 1374; preliminary report, H. Ogura, H. Takayanagi, K. Furuhata, and Y. Iitaka, *J.C.S. Chem. Comm.*, 1974, 759.
[2] W. Bonthrone, F. S. Skelton, and D. H. Reid, 'Nuclear Magnetic Resonance in Chemistry,' ed. B. Pesce, Academic Press, New York, 1965, p. 263.
[3] D. H. Reid, F. S. Skelton, and W. Bonthrone, *Tetrahedron Letters*, 1964, 1797.
[4] R. M. Acheson, M. W. Foxton, and G. R. Miller, *J. Chem. Soc.*, 1965, 3200.
[5] P. J. Abbott, R. M. Acheson, U. Eisner, D. J. Watkin, and J. R. Carruthers, *J.C.S. Chem. Comm.*, 1975, 155.
[6] L. F. Johnson and W. C. Jankowski, 'Carbon-13 NMR Spectra,' Wiley, New York, 1972.

results. The structure was confirmed by ^1H and ^{13}C (Table 1) data. Compound (8) gives no ^{13}C absorption at *ca.* 50 p.p.m. (other than $CO_2{\cdot}CH_3$) assignable to an sp^3-hybridised carbon atom. The resonance assigned to C-4a was observed in CD_3NO_2 at 75.6 p.p.m. and is at



SCHEME 1

low field because of the presence of adjacent nitrogen and sulphur atoms.

Mass spectra of compounds (6) and (8) revealed similar fragmentations, with the fragment *m/e* 360 ($M - CO_2{\cdot}CH_3$) as the base peak. The compositions of the main fragments were confirmed by high-resolution measurements (see Supplementary Publication).

Further confirmation of structure (8) was provided by an *X*-ray analysis. The crystals were obtained from ethanol as yellow needles, m.p. 225—227° (monoclinic, $a = 13.69_5$, $b = 6.60_1$, $c = 20.58_0$ Å, $\beta = 100.0_4°$, space group $P2_1/c$), and there are four molecules in the unit cell. Intensity data were collected as for compound (6). A total of 1 920 independent structure factors out of the 2 520 theoretically possible were obtained. The structure was solved by using the symbolic addition method and was refined by the block-diagonal least-squares method to a final *R* value of 0.069. Bond lengths and angles are given in Table 4.

The mechanism of these reactions may be represented as shown in Scheme 2. The reaction in methanol is thought to involve the successive addition of two molecules of dimethyl acetylenedicarboxylate to benzothiazole, leading first to an ylide intermediate (A). Subsequent 1,4-dipolar cycloaddition of the second molecule gives (6'), which rapidly isomerizes to (6). This is suggested by the similarity to the adduct of pyridine and

TABLE 1

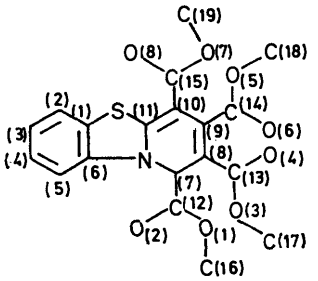
^{13}C N.m.r. data of compounds (6)—(8) (δ values)

Compd.	C-1	C-2	C-3	C-4	C-4a	C-5	C-5a	C-6	C-7	C-8	C-8a	C-9	C-9a	CO_2CH_3	CO_2CH_3	CHO
(6) [a]	55.6	140.7	161.1	100.8	161.3		128.2	122.2	127.0	124.6		111.1	138.8	164.0	51.8	
														164.6	52.3	
														167.5	52.5	
														167.7	53.2	
(7) [a]			53.1(2)		133.7	120.4		125.7	126.4	127.2	122.3			167.5	42.5	161.4
														169.0	51.1	
(8) [b]	141.7	110.3	138.8	103.9	75.6		129.4	127.7	127.6	123.9		110.3	140.3	165.3(2)	52.4	
														168.0	53.0(2)	
														170.2	54.4	

[a] In $CDCl_3$. [b] In CD_3NO_2; some assignments can be interchanged

TABLE 2

Data from *X*-ray analysis of compound (6)



(6)

(a) Bond lengths (Å) with e.s.d.s in parentheses

Bond	Length	Bond	Length
C(1)–C(2)	1.398(12)	C(10)–C(15)	1.457(9)
C(1)–C(6)	1.390(7)	C(11)–C(10)	1.393(12)
C(1)–S	1.750(8)	C(11)–N	1.359(8)
C(2)–C(3)	1.411(12)	C(12)–O(1)	1.241(11)
C(3)–C(4)	1.379(9)	C(12)–O(2)	1.223(13)
C(4)–C(5)	1.421(13)	C(13)–O(3)	1.341(8)
C(5)–C(6)	1.398(11)	C(13)–O(4)	1.202(9)
C(6)–N	1.404(11)	C(14)–O(5)	1.348(9)
C(7)–C(12)	1.539(8)	C(14)–O(6)	1.189(6)
C(7)–N	1.459(7)	C(15)–O(7)	1.349(11)
C(8)–C(7)	1.512(11)	C(15)–O(8)	1.195(7)
C(8)–C(13)	1.470(7)	C(16)–O(1)	1.513(9)
C(9)–C(8)	1.360(9)	C(17)–O(3)	1.457(7)
C(9)–C(14)	1.507(10)	C(18)–O(5)	1.461(14)
C(10)–C(9)	1.435(7)	C(19)–O(7)	1.461(11)
C(11)–S	1.730(7)		

(b) Bond angles (°) with e.s.d.s in parentheses

Bond	Angle	Bond	Angle
C(2)–C(1)–C(6)	121.8(6)	C(8)–C(7)–N	109.2(5)
C(3)–C(2)–C(1)	116.4(7)	O(2)–C(12)–C(7)	120.1(8)
C(4)–C(3)–C(2)	122.0(7)	O(2)–C(12)–O(1)	121.7(8)
C(5)–C(4)–C(3)	121.6(7)	C(7)–C(12)–O(1)	118.2(7)
C(6)–C(5)–C(4)	116.0(6)	O(3)–C(13)–C(8)	122.0(5)
N–C(6)–C(1)	111.5(5)	O(3)–C(13)–O(4)	123.1(6)
N–C(6)–C(5)	126.4(6)	C(8)–C(13)–O(4)	124.9(6)
C(1)–C(6)–C(5)	122.1(6)	O(5)–C(14)–C(9)	110.7(5)
C(10)–C(11)–N	120.9(6)	O(5)–C(14)–O(6)	125.2(6)
C(9)–C(10)–C(11)	116.6(6)	C(9)–C(14)–O(6)	124.1(6)
C(9)–C(10)–C(15)	125.6(6)	O(7)–C(15)–C(10)	111.9(6)
C(11)–C(10)–C(15)	117.3(6)	O(7)–C(15)–O(8)	122.9(6)
C(8)–C(9)–C(10)	121.1(6)	C(10)–C(15)–O(8)	125.2(6)
C(8)–C(9)–C(14)	120.1(6)	C(6)–N–C(11)	114.2(5)
C(10)–C(9)–C(14)	118.3(5)	C(6)–N–C(7)	123.9(5)
C(7)–C(8)–C(9)	119.5(6)	C(11)–N–C(7)	121.4(5)
C(7)–C(8)–C(13)	118.9(5)	C(12)–O(1)–C(16)	114.5(7)
C(9)–C(8)–C(13)	121.6(6)	C(13)–O(3)–C(17)	115.4(5)
C(12)–C(7)–C(8)	113.6(5)	C(14)–O(5)–C(18)	114.3(6)
C(12)–C(7)–N	108.0(5)	C(15)–O(7)–C(19)	116.7(6)

(c) Final atomic parameters (e.s.d.s in parentheses); anisotropic temperature factors ($\times 10^4$) of the form: $\exp(-B_{11}h^2 - B_{22}k^2 - B_{33}l^2 - B_{12}hk - B_{13}hl - B_{23}kl)$

Atom	*x/a*	*y/b*	*z/c*	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
C(1)	0.2859(7)	0.3521(6)	0.2192(5)	94(8)	89(8)	70(6)	38(7)	20(6)	−8(5)
C(2)	0.2472(7)	0.4679(7)	0.2160(7)	120(10)	95(9)	108(8)	54(8)	22(7)	−8(6)
C(3)	0.1302(8)	0.4240(8)	0.2805(7)	139(11)	129(10)	119(8)	77(9)	34(8)	−10(7)
C(4)	0.0569(8)	0.2766(8)	0.3426(7)	154(11)	125(10)	106(8)	84(9)	35(7)	−11(7)
C(5)	0.0977(7)	0.1604(7)	0.3472(6)	113(9)	118(9)	89(7)	55(8)	37(6)	−11(6)
C(6)	0.2167(7)	0.2049(6)	0.2860(5)	106(8)	92(8)	66(6)	53(7)	15(6)	−12(5)
C(7)	0.2126(6)	−0.0538(6)	0.3233(5)	89(8)	76(7)	72(6)	36(6)	21(5)	−10(5)
C(8)	0.3395(6)	−0.1054(6)	0.3594(5)	95(8)	80(7)	63(5)	35(6)	17(5)	−17(5)
C(9)	0.4575(6)	−0.0290(6)	0.2961(5)	84(7)	70(7)	65(5)	24(6)	14(5)	−24(5)
C(10)	0.4729(6)	0.1095(6)	0.2055(6)	96(8)	89(7)	61(5)	34(6)	26(5)	−14(5)
C(11)	0.3915(6)	0.1834(6)	0.2116(5)	84(8)	81(7)	56(5)	29(6)	16(5)	−9(5)
C(12)	0.0751(7)	−0.1300(7)	0.2170(7)	95(9)	113(9)	125(8)	19(8)	9(7)	−47(7)
C(13)	0.3346(7)	−0.2346(6)	0.4651(6)	104(8)	71(7)	73(6)	34(6)	19(6)	−12(5)
C(14)	0.5859(7)	−0.0777(6)	0.3320(6)	102(8)	84(8)	73(6)	34(7)	31(6)	−15(5)
C(15)	0.5804(7)	0.1885(6)	0.1197(6)	109(9)	83(8)	70(6)	31(7)	31(6)	−11(5)
C(16)	−0.0899(11)	−0.3253(10)	0.0994(9)	208(16)	196(15)	143(11)	35(13)	−34(11)	−70(11)
C(17)	0.1857(8)	−0.4353(7)	0.6081(7)	138(10)	99(9)	93(7)	42(8)	42(7)	30(6)
C(18)	0.6504(10)	−0.2666(11)	0.3232(11)	186(15)	205(16)	326(19)	135(14)	−3(14)	−129(14)
C(19)	0.7566(9)	0.1708(9)	0.0343(7)	181(13)	180(12)	113(8)	83(11)	93(9)	0(8)
O(1)	0.0545(6)	−0.2532(6)	0.1992(5)	225(10)	140(8)	110(6)	88(8)	−43(6)	−59(5)
O(2)	−0.0118(9)	−0.0703(10)	0.1539(9)	299(16)	399(18)	376(16)	251(15)	−191(13)	−276(15)
O(3)	0.1988(5)	−0.3075(4)	0.5017(4)	112(6)	94(6)	77(4)	53(5)	35(4)	14(4)
O(4)	0.4385(5)	−0.2726(5)	0.5137(4)	108(6)	117(7)	115(5)	52(5)	39(5)	19(5)
O(5)	0.5383(5)	−0.2023(5)	0.2824(5)	102(6)	106(6)	142(6)	43(5)	14(5)	−62(5)
O(6)	0.7109(5)	−0.0153(5)	0.3968(4)	87(6)	111(6)	88(5)	27(5)	12(4)	−30(4)
O(7)	0.6439(5)	0.1017(5)	0.1152(4)	172(8)	147(7)	91(5)	86(6)	70(5)	4(5)
O(8)	0.6081(6)	0.3137(5)	0.0574(4)	178(8)	121(7)	107(5)	66(6)	81(5)	13(5)
S	0.4237(2)	0.3709(2)	0.1462(1)	93(2)	75(2)	72(1)	30(2)	29(1)	2(1)
N	0.2775(5)	0.1112(5)	0.2788(4)	91(7)	71(6)	63(5)	35(5)	24(4)	−5(4)

dimethyl acetylenedicarboxylate.[7-9] A possible mechanism for the formation of the benzothiazine compound (7) in methanol is also shown in Scheme 2.

EXPERIMENTAL

M.p.s were measured for samples in capillary tubes. ^{1}H N.m.r. spectra were measured for solutions in $CDCl_3$ with a Varian T-60 spectrometer, ^{13}C n.m.r. spectra with a Varian HA-100 or JEOL PS 100-PFT spectrometers, with Me_4Si as internal standard, and mass spectra with a JEOL-O1S spectrometer (by direct insertion and at 75 eV).

† For details of Supplementary Publications see Notice to Authors No. 7, *J.C.S. Perkin I*, 1974, Index issue.

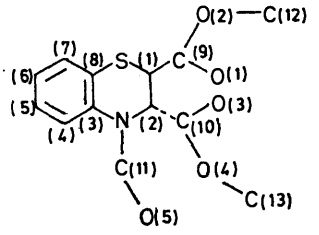
Crystallographic structure factor tables and mass spectral data for compounds (6)—(8) are available as Supplementary Publication No. SUP 21534 (28 pp., 1 microfiche).†

Reaction of Benzothiazole with Dimethyl Acetylenedicarboxylate in Methanol.—To a solution of benzothiazole (2 g) in methanol (20 ml), dimethyl acetylenedicarboxylate (4.2 g) was added. After 5 days at room temperature the methanol was evaporated off under reduced pressure. Chromatography (CCl_4–$CHCl_3$, 1 : 1) of the remaining tar afforded yellow prisms (0.29 g, 5%) of *tetramethyl* 1H-*pyrido*[2,1-b]-*benzothiazole*-1,2,3,4-*tetracarboxylate* (6), m.p. 239—240°

[7] R. M. Acheson and G. A. Taylor, *J. Chem. Soc.*, 1960, 1691.
[8] R. M. Acheson and A. O. Plunkett, *J. Chem. Soc.*, 1964, 2676.
[9] R. M. Acheson, *Adv. Heterocyclic Chem.*, 1963, **1**, 125.

TABLE 3

Data from *X*-ray analysis of compound (7)



(7)

(a) Bond lengths (Å) and angles (°) with e.s.d.s in parentheses

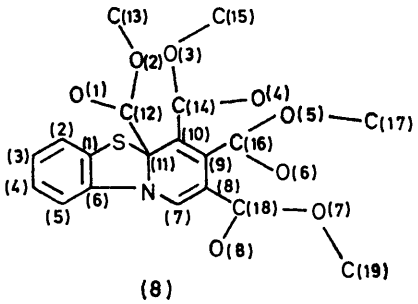
Bond	Length	Bond	Length	Bond	Angle	Bond	Angle
C(1)–C(2)	1.540(6)	C(7)–C(8)	1.408(8)	C(1)–C(2)–C(10)	110.9(4)	C(4)–C(5)–C(6)	119.5(6)
C(1)–C(9)	1.518(9)	C(8)–S	1.757(6)	C(1)–C(2)–N	111.9(4)	C(4)–C(3)–N	119.7(5)
C(1)–S	1.817(5)	C(9)–O(1)	1.205(9)	C(1)–S–C(8)	102.6(2)	C(4)–C(3)–C(8)	119.7(5)
C(2)–N	1.461(8)	C(9)–O(2)	1.329(6)	C(1)–C(9)–O(1)	125.3(5)	C(5)–C(6)–C(7)	120.2(6)
C(2)–C(10)	1.502(9)	C(10)–O(3)	1.205(9)	C(1)–C(9)–O(2)	110.5(5)	C(6)–C(7)–C(8)	120.1(6)
C(3)–N	1.425(6)	C(10)–O(4)	1.328(6)	C(2)–C(1)–C(9)	111.4(4)	C(7)–C(8)–S	115.2(4)
C(3)–C(4)	1.399(8)	C(11)–O(5)	1.228(7)	C(2)–C(10)–O(3)	123.5(5)	C(8)–C(3)–N	120.4(4)
C(3)–C(8)	1.407(7)	C(11)–N	1.377(8)	C(2)–N–C(3)	121.8(4)	C(9)–O(2)–C(12)	115.2(5)
C(4)–C(5)	1.409(9)	C(12)–O(2)	1.492(10)	C(2)–N–C(11)	118.3(4)	C(9)–C(1)–S	111.1(3)
C(5)–C(6)	1.404(9)	C(13)–O(4)	1.473(10)	C(2)–C(1)–S	111.2(3)	C(10)–O(4)–C(13)	116.1(5)
C(6)–C(7)	1.393(10)			C(2)–C(10)–O(4)	112.0(4)	C(10)–C(2)–N	114.2(4)
				C(3)–C(8)–C(7)	119.8(5)	O(1)–C(9)–O(2)	124.0(5)
				C(3)–C(8)–S	124.9(4)	O(3)–C(10)–O(4)	124.1(5)
				C(3)–C(4)–C(5)	120.3(5)	O(5)–C(11)–N	123.0(5)
				C(3)–N–C(11)	119.1(4)		

(b) Final atomic parameters (e.s.d.s in parentheses); anisotropic temperature factors ($\times 10^4$) of the form: $\exp(-B_{11}h^2 - B_{22}k^2 - B_{33}l^2 - B_{12}hk - B_{13}hl - B_{23}kl)$

Atom	*x/a*	*y/b*	*z/c*	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
C(1)	0.1628(7)	0.2276(5)	1.0785(7)	109(10)	44(4)	76(9)	3(5)	25(7)	−11(5)
C(2)	−0.0023(7)	0.1803(5)	0.9224(7)	90(9)	47(4)	63(9)	10(5)	29(7)	−8(5)
C(3)	0.1079(6)	0.3027(4)	0.6905(6)	89(8)	38(4)	72(8)	9(4)	36(7)	−4(4)
C(4)	0.0779(8)	0.3232(5)	0.5077(8)	158(12)	61(5)	94(10)	31(6)	62(9)	6(6)
C(5)	0.1556(10)	0.4320(6)	0.4442(9)	217(15)	67(6)	150(13)	38(7)	112(12)	23(7)
C(6)	0.2601(10)	0.5211(6)	0.5651(10)	206(15)	61(6)	190(15)	26(7)	120(12)	24(7)
C(7)	0.2834(8)	0.5035(5)	0.7463(9)	146(12)	47(5)	158(13)	6(6)	76(10)	4(6)
C(8)	0.2083(7)	0.3939(5)	0.8103(7)	103(9)	42(4)	87(9)	6(5)	36(7)	−6(5)
C(9)	0.3076(7)	0.1492(5)	1.1143(7)	100(10)	68(5)	91(10)	6(6)	24(8)	2(6)
C(10)	−0.1592(7)	0.2368(5)	0.9180(7)	109(10)	49(4)	109(10)	11(5)	50(8)	−3(5)
C(11)	0.0162(8)	0.0858(5)	0.6663(8)	164(12)	47(5)	103(10)	4(6)	50(9)	−25(5)
C(12)	0.5869(10)	0.1074(8)	1.3149(11)	143(14)	131(9)	215(18)	57(9)	−25(12)	1(10)
C(13)	−0.4520(9)	0.2692(8)	0.7457(11)	118(13)	137(9)	240(18)	62(9)	67(12)	18(10)
O(1)	0.3056(6)	0.0690(5)	1.0215(6)	160(9)	99(5)	153(10)	53(5)	16(7)	−38(5)
O(2)	0.4359(6)	0.1781(4)	1.2670(6)	134(9)	94(5)	131(9)	24(5)	−27(7)	−21(5)
O(3)	−0.1766(6)	0.2730(5)	1.0482(6)	181(10)	115(5)	146(9)	45(6)	69(8)	−44(6)
O(4)	−0.2824(5)	0.2323(4)	0.7575(5)	105(7)	85(4)	118(8)	29(4)	35(6)	−2(5)
O(5)	−0.0556(7)	−0.0130(4)	0.7063(6)	253(11)	46(3)	133(9)	−23(5)	94(8)	−29(4)
S	0.2434(2)	0.3859(1)	1.0405(2)	176(3)	47(1)	83(2)	−17(1)	29(2)	−21(1)
N	0.0332(6)	0.1907(4)	0.7535(5)	108(8)	36(3)	67(7)	1(4)	39(6)	−14(4)

TABLE 4

Data from *X*-ray analysis of compound (8)



(8)

(a) Bond lengths (Å) with e.s.d.s in parentheses

Bond	Length	Bond	Length
C(1)–C(2)	1.390(12)	C(11)–C(12)	1.536(11)
C(1)–C(6)	1.392(12)	C(11)–S	1.847(9)
C(1)–S	1.754(7)	C(11)–N	1.487(9)
C(2)–C(3)	1.408(11)	C(12)–O(1)	1.193(10)
C(3)–C(4)	1.388(13)	C(12)–O(2)	1.320(9)
C(4)–C(5)	1.399(13)	C(13)–O(2)	1.487(12)
C(5)–C(6)	1.390(10)	C(14)–O(3)	1.347(10)
C(6)–N	1.419(10)	C(14)–O(4)	1.200(10)
C(7)–C(8)	1.360(11)	C(15)–O(3)	1.462(10)
C(7)–N	1.354(11)	C(16)–O(5)	1.320(9)
C(8)–C(9)	1.455(10)	C(16)–O(6)	1.193(10)
C(8)–C(18)	1.487(11)	C(17)–O(5)	1.450(10)
C(9)–C(10)	1.355(11)	C(18)–O(7)	1.322(9)
C(9)–C(16)	1.500(11)	C(18)–O(8)	1.200(9)
C(10)–C(11)	1.514(11)	C(19)–O(7)	1.457(11)
C(10)–C(14)	1.487(10)		

(b) Bond angles (°) with e.s.d.s in parentheses

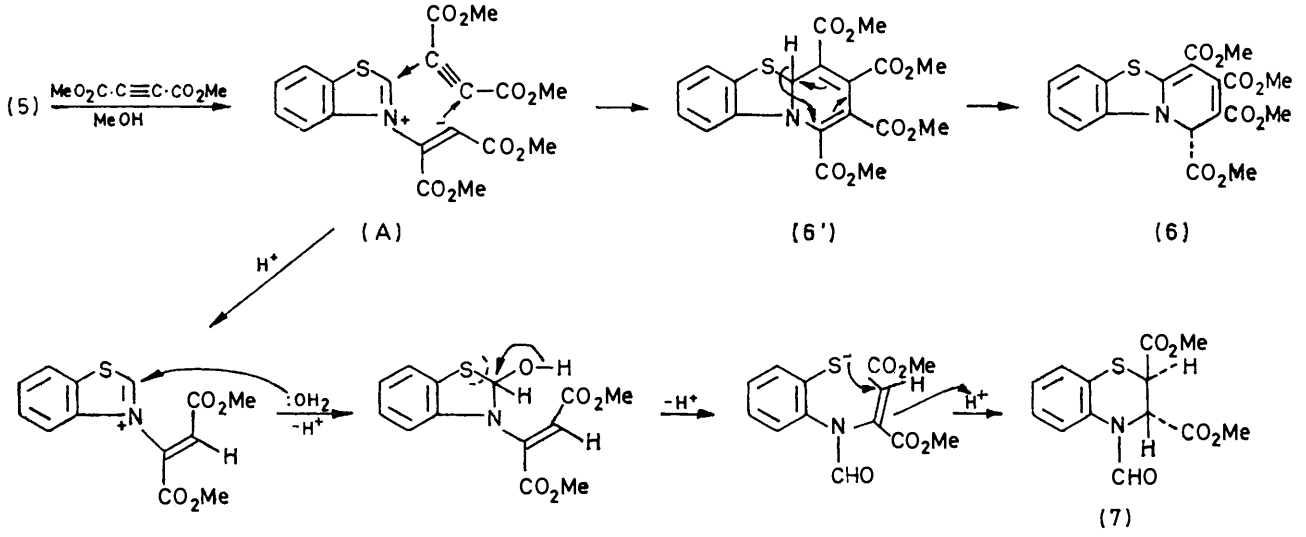
Bond	Angle	Bond	Angle
C(2)–C(1)–C(6)	120.7(7)	C(10)–C(11)–S	113.9(5)
C(2)–C(1)–S	126.1(6)	C(10)–C(11)–N	108.3(6)
C(6)–C(1)–S	112.9(5)	S–C(11)–N	104.4(4)
C(3)–C(2)–C(1)	118.1(7)	O(1)–C(12)–C(11)	124.2(7)
C(4)–C(3)–C(2)	120.4(8)	O(1)–C(12)–O(2)	124.3(7)
C(5)–C(4)–C(3)	121.5(8)	C(11)–C(12)–O(2)	111.3(6)
C(6)–C(5)–C(4)	117.4(7)	O(3)–C(14)–C(10)	110.8(6)
N–C(6)–C(1)	112.8(6)	O(3)–C(14)–O(4)	123.9(7)
N–C(6)–C(5)	125.4(7)	C(10)–C(14)–O(4)	125.1(7)
C(1)–C(6)–C(5)	121.6(7)	O(5)–C(16)–C(19)	111.4(6)
C(8)–C(7)–N	119.6(7)	O(5)–C(16)–O(6)	125.4(7)
C(9)–C(8)–C(7)	119.2(7)	C(9)–C(16)–O(6)	123.0(7)
C(9)–C(8)–C(18)	123.4(6)	O(7)–C(18)–C(8)	111.4(6)
C(7)–C(8)–C(18)	116.6(7)	O(7)–C(18)–O(8)	124.9(7)
C(10)–C(9)–C(8)	119.0(6)	C(8)–C(18)–O(8)	123.6(7)
C(10)–C(9)–C(16)	120.1(6)	C(1)–S–C(11)	91.6(3)
C(8)–C(9)–C(16)	120.4(6)	C(6)–N–C(7)	126.8(6)
C(11)–C(10)–C(9)	118.0(6)	C(6)–N–C(11)	114.1(6)
C(11)–C(10)–C(14)	120.6(6)	C(7)–N–C(11)	118.6(6)
C(9)–C(10)–C(14)	121.3(6)	C(12)–O(2)–C(13)	116.1(6)
C(12)–C(11)–C(10)	114.1(6)	C(14)–O(3)–C(15)	116.2(6)
C(12)–C(11)–S	107.9(5)	C(16)–O(5)–C(17)	116.0(6)
C(12)–C(11)–N	107.3(6)	C(18)–O(7)–C(19)	116.4(6)

(c) Final atomic parameters (e.s.d.s in parentheses); anisotropic temperature factors ($\times 10^4$) of the form: $\exp(-B_{11}h^2 - B_{22}k^2 - B_{33}l^2 - B_{12}hk - B_{13}hl - B_{23}kl)$

Atom	*x/a*	*y/b*	*z/c*	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
C(1)	0.2695(6)	0.2752(13)	0.5154(4)	31(5)	121(21)	12(2)	−10(9)	5(2)	0(6)
C(2)	0.2858(6)	0.1255(14)	0.5636(4)	43(6)	152(25)	13(2)	9(10)	6(3)	7(6)
C(3)	0.3640(6)	0.1532(14)	0.6171(4)	44(6)	157(25)	14(2)	11(10)	3(3)	8(6)
C(4)	0.4237(7)	0.3241(15)	0.6206(4)	40(6)	175(26)	19(2)	6(10)	3(3)	15(7)
C(5)	0.4082(6)	0.4737(14)	0.5717(4)	35(5)	162(25)	12(2)	−6(10)	1(3)	1(6)
C(6)	0.3304(6)	0.4451(13)	0.5194(4)	26(5)	113(22)	12(2)	−1(8)	1(3)	6(6)
C(7)	0.3542(6)	0.7466(13)	0.4519(4)	28(4)	98(20)	15(2)	1(9)	3(2)	2(6)
C(8)	0.3330(5)	0.8341(12)	0.3913(4)	19(4)	106(20)	14(2)	−11(8)	0(2)	1(6)
C(9)	0.2738(5)	0.7227(12)	0.3372(4)	24(4)	106(21)	11(2)	4(8)	2(2)	−3(6)
C(10)	0.2168(5)	0.5665(12)	0.3513(3)	19(4)	136(22)	9(2)	4(8)	2(2)	−3(6)
C(11)	0.2076(5)	0.5322(12)	0.4227(4)	15(4)	130(22)	11(2)	−12(8)	3(2)	0(5)
C(12)	0.1299(6)	0.6670(13)	0.4470(4)	27(5)	147(23)	11(2)	−14(8)	5(2)	−4(6)
C(13)	−0.0302(6)	0.8174(17)	0.4186(5)	33(6)	326(36)	24(3)	52(12)	10(3)	−12(8)
C(14)	0.1633(6)	0.4338(12)	0.2984(4)	31(5)	77(20)	15(2)	−4(8)	−4(3)	−4(6)
C(15)	0.0382(6)	0.1793(14)	0.2756(4)	38(5)	147(24)	20(2)	−31(10)	−1(3)	−21(7)
C(16)	0.2849(6)	0.7637(13)	0.2672(4)	37(5)	90(20)	13(2)	−19(9)	7(3)	−7(6)
C(17)	0.2043(7)	0.8805(19)	0.1638(4)	59(7)	402(40)	9(2)	25(14)	5(3)	21(8)
C(18)	0.3849(6)	1.0270(12)	0.3821(4)	31(5)	99(21)	11(2)	−2(8)	3(3)	0(6)
C(19)	0.4149(7)	1.2721(14)	0.3041(4)	54(6)	123(24)	24(3)	−25(11)	4(3)	23(7)
O(1)	0.1368(5)	0.7294(12)	0.5020(3)	51(4)	330(23)	14(2)	28(9)	0(2)	−27(5)
O(2)	0.0532(4)	0.7002(10)	0.3996(3)	36(3)	209(19)	13(1)	23(7)	−1(2)	−11(4)
O(3)	0.0865(4)	0.3998 (9)	0.3186(3)	30(3)	141(16)	16(2)	−26(6)	2(2)	−10(4)
O(4)	0.1832(4)	0.4163(9)	0.2441(3)	42(4)	172(17)	12(1)	−14(7)	4(2)	−9(4)
O(5)	0.2044(4)	0.8482(9)	0.2334(3)	34(3)	143(15)	12(1)	12(6)	2(2)	11(4)
O(6)	0.3578(4)	0.7216(9)	0.2457(3)	36(3)	172(17)	16(2)	1(7)	10(2)	2(4)
O(7)	0.3607(4)	1.0951(9)	0.3210(3)	51(4)	136(16)	13(1)	−27(7)	−2(2)	7(4)
O(8)	0.4416(4)	1.1088(9)	0.4252(3)	44(4)	163(17)	16(2)	−28(7)	−3(2)	1(4)
S	0.1818(2)	0.2667(3)	0.4423(1)	34(1)	111(5)	12(0)	−23(2)	0(1)	1(2)
N	0.3050(4)	0.5773(10)	0.4646(3)	22(4)	132(19)	9(2)	−9(2)	1(2)	4(5)

(from methanol) (245—247° on a Reichert hot-stage apparatus), $\nu_{max.}$ (KBr) 1 736, 1 712, 1 659 (CO_2CH_3), 1 583, and 751 cm^{-1} (Ph), $\lambda_{max.}$ (EtOH) 228 (log ε 4.26), 259 (4.04), 309 (4.22), and 414 nm (4.15), δ_H 3.69, 3.82, 3.85, and 3.93 (12 H, s, 4 × CO_2Me), 6.43 (1 H, s, CH), and 7.3—7.8 (4 H, m, ArH) (Found: C, 54.15; H, 4.05; N, 3.05. $C_{19}H_{17}NO_8S$ requires C, 54.4; H, 4.1; N, 3.35%).

thiazole (1 g) in dimethylformamide (8 ml), dimethyl acetylenedicarboxylate (2.1 g) was added. After 5 days at room temperature, the organic solvent was removed under reduced pressure. Crystallization from methanol gave *tetramethyl 4aH-pyrido*[2,1-b]*benzothiazole*-2,3,4,4a-*tetracarboxylate* (8) as yellow needles (0.6 g, 10%), m.p. 225—227° (m.p. and mixed m.p. with authentic sample [5] 233—



SCHEME 2

From the mother liquor of (6), *dimethyl 4-formyl*-2,3-*dihydro*-1,4-*benzothiazine*-2,3-*dicarboxylate* (7) was obtained as colourless prisms (0.37 g, 8%), m.p. 135—136°, $\nu_{max.}$ (KBr) 1 740 (CO_2CH_3), 1 690 (CHO), 1 575, and 715 cm^{-1} (Ph), $\lambda_{max.}$ (EtOH) 229 (log ε 4.28), 258sh (3.86), and 299 nm (2.90), δ_H 3.72 and 3.76 (6 H, s, 2 × CO_2Me), 4.50 and 6.14 (2 H, dd, *J* 3.8 Hz, 2 × CH), 7.20br (s, ArH), and 8.75 (1 H, s, CHO) (Found: C, 52.75; H, 4.5; N, 4.65. $C_{18}H_{18}NO_8S$ requires C, 52.85; H, 4.45; N, 4.75%).

Reaction of Benzothiazole with Dimethyl Acetylenedicarboxylate in Dimethylformamide.—To a solution of benzo-

234° on a Reichert hot-stage apparatus), $\nu_{max.}$ (KBr) 1 738, 1 717, and 1 703 (CO_2CH_3), 1 598, and 765 cm^{-1} (Ph), $\lambda_{max.}$ (EtOH) 221 (log ε 4.11), 270 (4.06), 299 (3.71), and 428 nm (3.65), δ_H 3.70, 3.79, 3.84, and 3.92 (12 H, s, 4 × CO_2Me), 7.2—7.3 (4 H, m, ArH), and 8.49 (1 H, s, 2-H) (Found: C, 54.35; H, 4.2; N, 3.05. $C_{19}H_{17}NO_8S$ requires C, 54.4; H, 4.1; N, 3.35%).

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