PROTON MAGNETIC RESONANCE SPECTRA OF SOME 1,2-DITHIOLE-3-ONES AND 1,2-DITHIOLE-3-THIONES

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Summary

P.m.r. spectra of 31 derivatives in the title series are tabulated. The chemical shifts of the heterocyclic ring protons, the influence of substituents upon them, the differences between the two systems, and allylic coupling in methyl derivatives are discussed. It was not found possible to make any firm conclusion regarding aromaticity of these systems, but there is some evidence that the bond order of C 4–C 5 bond is less than 2.

The p.m.r. spectra of a number of simple aniline derivatives were examined as model compounds. Acetylation of the amino groups causes a downfield shift (0·7–2·2 p.p.m.) in the *ortho* ring protons.

Introduction

In connection with another project[1,2] we had available a number of compounds in the title series. Because their p.m.r. spectra appeared to be of interest and because no systematic studies in this area have as yet appeared,[3–6] further compounds (cf.[7–15]) were obtained and their p.m.r. spectra determined. The spectra of the whole series are collected and discussed in this work.

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[1] Brown, R. F. C., and Rae, I. D., *Aust. J. Chem.*, 1964, **17**, 447.

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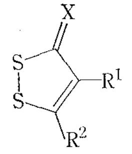
Aust. J. Chem., 1965, **18**, 1211–19

TABLE 1

P.M.R. DATA ON SOME 1,2-DITHIOLE-3-ONES AND 1,2-DITHIOLE-3-ONES

Chemical shifts are expressed in τ values. All resonances were of the expected multiplicity and relative intensity. The AA′BB′ multiplets are defined only in terms of the frequency (c/s ex TMS) of the four principal resonances

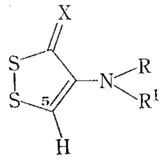


Compound	Ref.	X = O			Ref.	X = S		
		H 4	H 5	Other Resonances		H 4	H 5	Other Resonances
$R^1 = R^2 = H$	7	3·36 $J_{4,5}$	1·60 5·3 c/s	—	7,8	2·80 $J_{4,5}$	1·65 5·40 c/s	—
$R^2 = H, R^2 = Me$	9	3·60	—	7·52 (Me) $J_{H,Me}$ 1·08 c/s	10	3·00	—	7·52 (Me), $J_{H,Me}$ 0·97 c/s
$R^1 = Me, R^2 = H$	—	—	2·03	7·93 (Me) $J_{H,Me}$ 1·13 c/s	11	—	1·90	7·78 (Me), $J_{H,Me}$ 0·92 c/s
$R^1 = H, R^2 = COOEt$	12	2·70	—	quartet 5·55 and triplet 8·60 (OEt)	12	2·35	—	quartet 5·55 and triplet 8·60 (OEt)
$R^2 = H, R^1 = p\text{-}C_6H_4Me$	—	—	1·72	7·64 ($ArCH_3$); AA′BB′ 453, 444·5, 436, 428	13	—	1·62	7·61 ($ArCH_3$); AA′BB′ 451, 443, 438, 429
$R^1 = H, R^2 = p\text{-}C_6H_4OMe$	14	3·45	—	6·14 (OMe); AA′BB′ 459, 450, 422, 413	15	2·68	—	6·12 (Me); AA′BB′ 454·5, 462·5, 421·5, 412·5
$R^1 = Ph, R^2 = H$	—	—	1·64	broad 2·55 (Ph)	13	—	1·61	narrow 2·55 (Ph)
$R^1 = H, R^2 = Ph$	14	3·23	—	multiplet 2·50 (Ph)	15	2·65	—	multiplet 2·50 (Ph)

TABLE 2

P.M.R. DATA[2] ON 4-AMINO-1,2-DITHIOLE-3-ONE, 4-AMINO-1,2-DITHIOLE-3-THIONE, AND THEIR DERIVATIVES

Chemical shifts are expressed in τ values. All resonances were of the expected multiplicity and relative intensity



Compound	X = O		X = S		Ref.
	H 5	Other Resonances	H 5	Other Resonances	
$R = R^1 = H$	2·95	broad 6·0 (NH_2)	2·57	broad 5·5 (NH_2)	1
$R = H, R^1 = Me$	3·53	broad 5·80 (NH); 7·12 (N–Me)	3·03	5·28 (NH); 7·03 (NMe)	2
$R = H, R^1 = COPh$	0·70	broad 1·6 (NH); complex multiplet 1·9–2·6 (Ph)	0·30	broad 0·4 (NH); complex multiplet 1·8–2·5 (Ph)	1
$R = H, R^1 = COMe$	0·91	broad 2·15 (NH); 7·80 (COMe)	0·62	broad 1·5 (NH), 7·73 (COMe)	1
$R = H, R^1 = COCH_2COMe$	0·87	broad 0·9 (NH); 6·35 ($-CH_2-$); 7·66 ($COCH_3$)	0·65	broad 0·35 (NH); 6·32 ($-CH_2-$); 7·57 ($COCH_3$)*	1
$R = H, R^1 = COOCH_2Ph$	1·45	broad 2·8 (NH); 2·66 (Ph); 4·81 ($-CH_2-$)	1·05	broad 2·1 (NH); 2·66 (Ph); 4·78 ($-CH_2-$)	1
$R = H, R^1 = p\text{-}SO_2C_6H_4Me$	1·78	AA′BB′, 2·53 (HAr); broad 3·0 (NH); 7·61 ($ArCH_3$)	1·57	AA′BB′, 2·59 (HAr); broad 2·3 (NH); 7·61 ($ArCH_3$)	1
$R = Me, R^1 = p\text{-}SO_2C_6H_4Me$	1·46	AA′BB′, 2·59 (HAr); 6·83 (N–Me); 7·57 ($ArCH_3$)	1·32	AA′BB′, 2·50 (HAr); 6·72 (N–Me); 7·58 ($ArCH_3$)	2

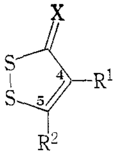
* A set of weak lines, assignable to the enolic form, was also present: 0·61 (H 5); 4·82 (=CH); 7·98 (=C–Me).

RESULTS AND DISCUSSION

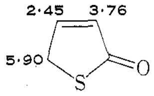
The p.m.r. data for the two parent systems (I; $R^1 = R^2 = H$, $X = O$) and (I; $R^1 = R^2 = H$, $X = S$) and a number of derivatives are given in Tables 1 and 2. The amino derivatives (Table 2) will be discussed separately (see below).

(i) *The Chemical Shifts of Ring Protons*

Although *purely* theoretical calculation of proton chemical shifts can at present be attempted only for the simplest systems,[16] it is recognized that shielding contributions may arise from charge density on the atom to which the proton is attached,[17] from long-range anisotropy effects,[18] electric field effects,[19] and proximity or dispersion effects.[20] Usually more than one of these effects is present, each of which may be separated into components due to various groups in the molecule. A quantitative estimate of the contributions of each effect is therefore unlikely to be reliable in the case of a heterocyclic system of the type discussed here, and it may be more profitable to discuss the chemical shifts of ring protons in 1,2-dithiole-3-ones (I; $X = O$) and 1,2-dithiole-3-thiones (I; $X = S$) in terms of model systems.



(I)



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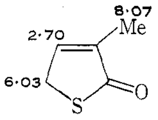

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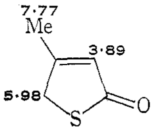

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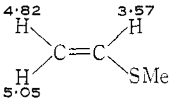

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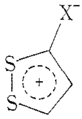

(VI)

The resonances of the ring proton in (I) (Table 1) occur at substantially lower field than those of cyclic olefins (cf. vinylic protons in cyclopentene τ 4·40)[21] as would be expected from the presence of conjugated carbonyl groups and of heteroatoms.[18] A possibly acceptable model system, particularly for the vinylic protons α to the

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[16] Kolker, H. J., and Karplus, M., *J. Chem. Phys.*, 1964, **41**, 1259; Hall, G. G., Hardisson, A., and Jackman, L. M., *Tetrahedron*, 1963, **19**(Suppl. 2), 101, and references therein.

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[21] Wiberg, K. B., and Nist, B. J., *J. Am. Chem. Soc.*, 1961, **83**, 1226.

carbonyl group in (I) (X = O) are the thiolactones (II), (III), and (IV)[22,23] although the influence of the second sulphur on the chemical shift of the α-protons (H 4) may be considerable as indicated by the comparison of the chemical shifts in ethylene (τ 4·72)[24] and methyl vinyl thioether (V)[25a]. Similarly, the β-protons, [R^2 = H in (I)] would be expected to resonate at lower fields than the β-proton in (II) owing to electron withdrawal by the –S–S– group.[26] Within the limits of validity of such corrections, it can be seen that the vinylic protons in (I) (X = O; $R^1 = R^2$ = H) have similar chemical shifts to those in (II).

While arguments of this sort assume additivity of chemical shifts (which does *not* generally apply except for series of very closely related compounds, e.g. Shoolery's rules[18]), they indicate that there is no *a priori* case for invoking ring current effects [(i.e. aromaticity of (I; X = O)] to explain the chemical shifts of the ring protons. Especially is this so because structures of the type (VI) which involve placing some positive charge on the ring, and hence further deshielding, could be expected to contribute to the resonance hybrid of (I) if it were aromatic.

Chemical shifts of ring protons in 3-isothiazolones[27,28] occur at very similar fields.

(ii) *Influence of Substituents on the Chemical Shifts of Ring Protons*

Table 1 shows that when either R^1 or R^2 in (I) is a methyl group, the remaining proton resonates upfield with respect to the same proton in the parent system.[24,29] It is noticeable that this shift is significantly smaller than the "total methyl shift" in various heterocyclic systems.[29]

The effect of the introduction of an ethoxycarbonyl group at C 5 is normal.[30]

Introduction of an aryl substituent may either shield or deshield a proton in the vicinal position, depending on the orientation of the benzene ring.[31] The data summarized in Table 1 show that introduction of an aryl group at either C 4 or C 5 causes only small changes in the chemical shifts of the remaining ring proton when compared to the parent system. This suggests that the aryl groups at either C 4 or C 5 in *both* systems (I; X = O and X = S) attain a similar degree of coplanarity (approximately 45°) with the heterocyclic ring.[31]

(iii) *The Differences between the Chemical Shifts of the Ring Protons in 1,2-Dithiole-3-ones and 1,2-Dithiole-3-thiones*

Tables 1 and 2 show that there are systematic differences between the chemical shifts of the ring protons in the two systems and that, while the magnitude of the effects

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[22] Jacobsen, H. J., Larsen, E. H., and Lawesson, S. O., *Tetrahedron*, 1963, **19**, 1867.

[23] Hörnfeldt, A. B., and Gronowitz, S., *Acta Chem. Scand.*, 1962, **16**, 789.

[24] Reddy, G. S., and Goldstein, J. H., *J. Am. Chem. Soc.*, 1961, **83**, 2045.

[25] Bhacca, N. S., Johnson, L. F., and Shoolery, J. N., "N.M.R. Spectra Catalogue." (*a*) No. 36; (*b*) No. 51. (Varian Associates: Palo Alto, Cal., 1962.)

[26] Pettit, G. R., Douglas, I. B., and Hill, R. A., *Canad. J. Chem.*, 1964, **42**, 2357.

[27] Leonard, N. J., and Wilson, G. E., *Tetrahedron Letters*, 1964, 1471.

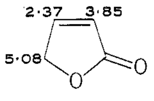
[28] Crow, W. D., and Leonard, N. J., *Tetrahedron Letters*, 1964, 1477.

[29] Reddy, G. S., and Goldstein, J. H., *J. Am. Chem. Soc.*, 1961, **83**, 5020.

[30] Jackman, L. M., and Wiley, R. H., *J. Chem. Soc.*, 1960, 2881, 2886.

[31] Inamotu, N., Masuoa, S., Nagai, Y., and Simamura, O., *J. Chem. Soc.* 1963, 1433, and references therein.

varies with the substitution pattern, the replacement of oxygen by sulphur in (I) is generally accompanied by downfield shifts in the resonances of the ring protons. Comparison of the model systems (II) and (VII)[25b] and of the series of pyrones and thiopyrones (VIII)–(XI)[32] indicates that the replacement of a carbonyl group by a thiocarbonyl group in cyclic conjugated systems appears to be associated with a paramagnetic shift of the α-protons and a lesser shift of the β-protons (as in the parent systems (I) (X = O) and (I) (X = S)). Substitution of *ring* oxygen by sulphur has generally less pronounced and less well-defined effects.



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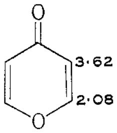

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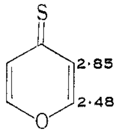

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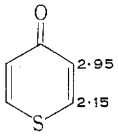
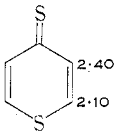


(X)



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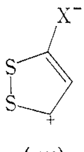

(XII)

Thus the differences in the ring proton shifts between (I) (X = O) and (I) (X = S) need not necessarily be due to differences in aromaticity. Further, if ring-current effects *only* were to be considered, the *differences* between the changes in chemical shifts in the two protons in the parent systems would be difficult to explain. However, the possible participation of charged structures (see above) makes this point difficult to evaluate.

(iv) *Allylic Coupling in Methyl Derivatives of (I)*

The allylic coupling constants between methyl groups and ring protons in the compounds investigated (Table 1) are in the range of 0·9–1·1 c/s, which is significantly less than those in other five-membered rings[33] with α,β unsaturated carbonyl or thiocarbonyl functions, e.g. in (III) and (IV) the allylic coupling constants[22,23] between the methyl groups and the vinylic protons four bonds away are 1·5 c/s. It has been suggested[33,34] that the magnitudes of allylic and *ortho*-benzylic[33–36] coupling constants reflect the bond orders in double bonds, and therefore the low allylic coupling constants in (I) can be taken as evidence for the bond order of the double bond in the ring being less than 2. However, it is not possible to distinguish

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[32] Bladon, P., and Brown, N. M. D., private communication.

[33] Sternhell, S., *Rev. Pure. Appl. Chem.*, 1964, **14**, 15.

[34] Rottendorf, H., and Sternhell, S., *Aust. J. Chem.*, 1964, **17**, 1315.

[35] Nair, P. M., and Gopakumar, G., *Tetrahedron Letters*, 1964, 709.

[36] Dewar, M. J. S., and Fahey, R. C., *J. Am. Chem. Soc.*, 1963, **85**, 2704.

between the attenuation of electron density in this double bond owing to participation of aromatic (closed loop) structure such as (VI) or to charged, non-aromatic structures with delocalized double bonds, such as (XII).

Differences between the allylic coupling constants in (I) (X = O) and (I) (X = S) are very small, but probably real, and could reflect some differences in bond order between C4 and C5.

The allylic coupling constant in (I) (X = O, R^1 = H, R^2 = CH_3) has been been previously reported[3] as 2·9 c/s. However, a carefully redetermined value from the same laboratory[37] was found to be 0·99 c/s, i.e. in reasonable agreement with the result given in Table 1. The comments made regarding the larger value in other communications[33,34] are no longer pertinent.

(v) *Ring Proton Shifts in the 4-Amino Derivatives*

It can be seen from examination of Table 2 that conversion of the 4-amino group in (I) to some of its derivatives causes large effects in the chemical shifts of H5. To test whether this effect was peculiar to the system (I), or general, we have examined the p.m.r. spectra of a number of simple anilines and their *N*-acetyl derivatives. It can be seen from Table 3 that *N*-acetylation causes considerable downfield shifts in all ring protons, as would be expected on general grounds, and has a particularly large effect on the *ortho* ring protons, presumably through long-range effects.[18,19] In addition, where a substituent *ortho* to the *N*-acetyl group is capable of forming a hydrogen bond to the amide proton, the resonances due to the remaining *ortho* proton are drastically shifted downfield (by up to 2·2 p.p.m.) and even the more remote *meta* protons are differentially affected. These data have obvious implications in structural analysis and may possibly be used for investigation of relative strength of H bonds. The extension to other aniline derivatives is under investigation, but it is already apparent that benzoylation and *N*-methylation have effects paralleling those observable in Table 2. The large (approximately 2 p.p.m.) downfield shifts (Table 2) in H5 associated with the conversion of (I) (X = O or S, R^1 = NH_2, R^2 = H) to the corresponding acetyl derivatives (I) (X = O or S, R^1 = NHCOMe, R^2 = H) suggests that hydrogen bonding between the amide proton and the C=O or C=S group is taking place. The larger downfield shifts for (I) (X = S) than for (I) (X = O) may reflect the greater size of the sulphur atom.[38]

EXPERIMENTAL

(a) *Preparation of Compounds*

The preparation of most of the substances used in this investigation has been described previously.[1,2] Other materials were prepared by similar methods (see below) or by routes described in the literature (see references in tables and text).

(i) *4-*p*-Tolyl-1,2-dithiol-3-one*

4-*p*-Tolyl-1,2-dithiole-3-thione[13] (1·90 g, 8·5 mmole) in chloroform (30 ml) was added to a cooled solution of mercuric acetate (6·3 g, 20 mmole) in glacial acetic acid (30 ml) and heated on the water-bath for 24 hr. The solution was diluted with benzene (100 ml) and washed with water,

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[37] Braillon, B., private communication.

[38] Hambly, A. N., and O'Grady, B. V., *Aust. J. Chem.*, 1964, **17**, 860.

TABLE 3

P.M.R. DATA ON SOME AMINES

Chemical shifts are in c/s ex TMS. Figures in brackets denote paramagnetic shift relative to the parent amine. s, singlet; b, broad signal. All resonances observed were of the expected relative intensity but those due to –NHCO– were often unobservable

Compound	H 2	H 3	H 4	H 5	H 6	Other Resonances
p-Methylaniline	378, 386*	402, 410*	—	cf. H 3	cf. H 2	s 202 (NH_2); s 134 (CH_3)
p-Methylacetanilide	440, 449* (63)	420, 429* (19)	—	cf. H 3	cf. H 2	s 137 (CH_3); s 126 ($COCH_3$)
p-Chloroaniline	391, 400*	423, 432*	—	cf. H 3	cf. H 2	s 212 (NH_2)
p-Chloroacetanilide	433, 441*† (42)	444, 453*† (21)	—	cf. H 3	cf. H 2	
p-Nitroaniline	393, 402*	480, 489*	—	cf. H 3	cf. H 2	
p-Nitroacetanilide	456, 465*† (62)	488, 497*† (8)	—	cf. H 3	cf. H 2	s 134 ($COCH_3$)
o-Methylaniline	—	‡	‡	‡	$\simeq$403	s 210 (NH_2); s 130 (CH_3)
o-Methylacetanilide	—	‡	‡	‡	$\simeq$448 ($\simeq$45)	b $\simeq$470 (NH); s 131 ($COCH_3$); s 124 (CH_3)
2,5-Dimethylaniline	—	405, 413	387,§ $\simeq$380	—	380§	b 196 (NH_2); s 131 (CH_3); s 123 (CH_3)
2,5-Dimethylacetanilide	—	419, 426·5 (14)	407, 415·5§ (29)	—	441§ (61)	b $\simeq$455 (NH); 3×s 124, 128, 136 (CH_3, $COCH_3$)
2,4-Dimethylaniline	—	408§	—	402, $\simeq$411§	381, 390	s 194 (NH_2); 2×s 132, 125 (CH_3)
2,4-Dimethylacetanilide	—	$\simeq$420§ ($\simeq$12)	—	411, $\simeq$420 (9)	437, 446 (56)	3×s 126, 130, 138 (CH_3, $COCH_3$)
2,5-Dichloroaniline	—	426, 434	394, $\simeq$402§	—	405§	s 240 (NH_2)
2,5-Dichloroacetanilide	—	433, 441 (7)	415, 424§ (22)	—	507§ (102)	s 133 ($COCH_3$)
2,5-Dimethoxyaniline	—	400, 408	371, $\simeq$379§	—	381§	s 226·5 (NH_2); 2×s 223, 228 (OMe)
2,5-Dimethoxyacetanilide	—	405, 414 (6)	389, 398§ (18)	—	487§ (106)	2×s 230, 227 (OMe); s 131 ($COCH_3$)
2,4-Dinitroaniline	—	551§	—	494, 503§	413, 422	
2,4-Dinitroacetanilide	—	551§ (0)	—	507, 516§ (13)	545, 554 (132)	s 143 ($COCH_3$)

* Part of AA′BB′ multiplet.

† The relative shift of H 2 (H 6) and H 3 (H 5) cannot be ascertained beyond doubt. The assignments given here were made on the basis of relative paramagnetic shifts compared with the parent amine.

‡ Part of complex multiplet.

§ Conspicuously broadened or narrow doublet (*meta* coupling).

sodium bicarbonate, and again with water, and the benzene was then evaporated. The resulting oil was chromatographed in benzene on silica gel to give the crude dithiolone (1·38 g, 78%) which was recrystallized from ethanol to give *4-p-tolyl-1,2-dithiol-3-one*, m.p. 86° (Found: C, 57·8; H, 4·1; S, 30·7. $C_{10}H_8OS_2$ requires C, 57·7; H, 3·9; S, 30·7%). Ultraviolet spectrum: λ_{max} 226, 242·5, 332 mμ; log ϵ_{max} 3·99, 4·05, 3·92. Infrared spectrum: 1632, 1550 cm^{-1}.

(ii) *4-Phenyl-1,2-dithiol-3-one*

Similar treatment of 4-phenyl-1,2-dithiole-3-thione[13] gave a 60% yield of *4-phenyl-1,2-dithiol-3-one*, m.p. 82–82·5° from ethanol (Found: C, 56·2; H, 3·3; S, 32·7. $C_9H_6OS_2$ requires C, 55·7; H, 3·1; S, 33·0%). Ultraviolet spectrum: λ_{max} 242, 329·5 mμ; log ϵ_{max} 3·95, 3·91. Infrared spectrum: 1640, 1540 cm^{-1}.

(iii) *5-Methyl-1,2-dithiol-3-one*

5-Methyl-1,2-dithiole-3-thione[10] (0·17 g) and mercuric acetate (1·00 g) were dissolved in 1:1 chloroform/acetic acid (10 ml) and heated on the water-bath for 1 hr. The solution was filtered, diluted with benzene (50 ml), and the neutral product worked up as above. The main fraction from chloroform/alumina chromatography was a colourless oil (24 g) which infrared, ultraviolet, and n.m.r. spectra (see Table 1) confirmed was 5-methyl-1,2-dithiol-3-one. Ultraviolet spectrum: λ_{max} 234·5, 304 mμ: log ϵ_{max} 3·47, 3·40. Infrared spectrum: 1670, 1578 cm^{-1}.

(iv) *4-Methyl-1,2-dithiol-3-one*

4-Methyl-1,2-dithiole-3-thione (174 mg) and mercuric acetate (0·50 g) were dissolved by warming in 1:1 chloroform/acetic acid. A pale yellow colloid formed as the solution was warmed on the water-bath and, after 10 min, this began to turn black. After 20 min no pale-coloured precipitate remained and the black precipitate had settled leaving an almost clear solution. The solution was worked up as described in the previous sections, and the resulting colourless oil was distilled at 50°/0·2 mm to give *4-methyl-1,2-dithiol-3-one* (72 mg, 47%) (Found: C, 37·5; H, 3·4; S, 46·8. $C_4H_4OS_2$ requires C, 36·4; H, 3·1; S, 48·4%). Despite the poor microanalysis spectral properties strongly supported the 4-methyldithiolone structure. Ultraviolet spectrum: λ_{max} 235·5, 311 mμ; logϵ 3·38, 3·78. Infrared spectrum: 1645, 1570 cm^{-1}.

(b) *P.M.R. Spectra*

All p.m.r. spectra were recorded on a Varian A60 spectrometer (60 Mc/s). Unless otherwise stated, the chemical shifts are quoted in τ values for dilute (1–5%) solutions in deuterochloroform. The coupling constants were generally determined for more concentrated (5–10%) solutions; all values of coupling constants (Table 1) are averages of 6–10 runs; the standard deviation (accuracy of measurement only) was approximately ±0·05 c/s. The doublets due to the methyl groups were resolved for approximately 70% of the height of the signal.

The accuracy of the sweep width was checked only for the 500 c/s sweep, using the separation between the singlets due to chloroform and tetramethylsilane (dilute solutions in carbon tetrachloride) which were always within 1 c/s of 436 c/s.

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