1115. *Two Dimers of Cyclohexanethione* *

By A. R. Katritzky, R. Mayer, J. Morgenstern, and M. J. Sewell

Two dimers of cyclohexanethione are shown by proton resonance spectroscopy to be 2,2:4,4-bispentamethylene-1,3-dithietan, and 2,2-pentamethylene-4,5-tetramethylene-1,3-dithiolan. The latter was shown to be the *cis*-isomer by independent synthesis of the *trans*-analogue.

Thioacetone dimer was mentioned by Wislicenus[1] before thioacetone itself had been characterised. This dimer, postulated and later investigated by many authors,[2-9] and its analogues, the dimers of methyl ethyl,[8] diethyl,[8] and di-n-propyl thioketone, were arbitrarily assigned 1,3-dithiacyclobutane structures(I).

Böhme, Pfeifer, and Schneider[10] were unable to confirm the existence of 2,2,4,4-tetramethyl-1,3-dithietan (I; $R^1 = R^2 = R^3 = R^4 =$ Me). However, they proposed the bicyclic dithietan structure (II) for the reaction product of chloroacetone and hydrogen sulphide (cf. also refs. 11, 12). Hromatka and Engel[13] rejected the dithietan formulation (II) for this compound in favour of 2,5-dimethyl-2,5-endosulphido-1,4-dithian (III).

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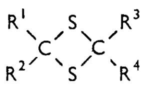
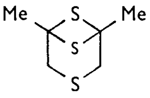
* Applications of Proton Resonance Spectroscopy to Structural Problems, Part XVIII. For Part XVII see A. R. Katritzky and R. E. Reavill, *Rec. Trav. chim.*, 1964, **83**, 1230.

[1] J. Wislicenus, *Z. Chem.*, 1869, **12**, 324.
[2] A. Claus, *Ber.*, 1875, **8**, 532.
[3] W. Spring, *Ber.*, 1881, **14**, 758.
[4] W. Spring, *Bull. Soc. chim. France*, 1883, **40**, (2), 66; cf. *Bull. Acad. roy. Med. Belg.*, 1883, **5**, [3], 236.
[5] B. Lach, *Ber.*, 1883, **16**, 1787.
[6] W. Autenrieth, *Ber.*, 1887, **20**, 373.
[7] E. Fromm and E. Baumann, *Ber.*, 1889, **22**, 1035.
[8] A. E. Kretow and Ya. F. Komissarow, *J. Gen. Chem.* (*U.S.S.R.*), 1935, **5**, (67), 388.
[9] S. Kambara, N. Yamazaki, and R. Niinomi, *J. Chem. Soc. Japan, Ind. Chem. Sect.*, 1951, **54**, 673.
[10] H. Böhme, H. Pfeifer, and E. Schneider, *Ber.*, 1942, **75**, 900.
[11] H. Brintzinger and H.-W. Ziegler, *Chem. Ber.*, 1948, **81**, 380.
[12] H. Böhme and E. Schneider, *Chem. Ber.*, 1949, **82**, 208.
[13] O. Hromatka and E. Engel, *Österr. Akad. Wiss. Wein, Math.-naturwiss. klasse Sitzungsber., Abt. IIb*, 1948, **157**, 38 (*Chem. Abs.*, 1949, **43**, 653).

Dithietan structures have also been proposed for thioacetoacetic ester dimer[14] and structure (IV)[15] has been suggested for the reaction product "anhydrotriacetophenone disulphide" from acetophenone and hydrogen sulphide. Later, the latter compound was identified[16] as 2,4-dimethyl-2,4,6-triphenyl-2*H*,4*H*-1,3-dithiin (V). Thiobenzophenone dimer[17] (see also ref. 18) and xanthione dimer[17] have been formulated with structures of type (I) but detailed investigations have not been carried out. Schönberg[19,20] found experimental evidence against the 1,3-dithietan structure for the well-known[17,21,22] thiofluorenone dimer.


(I)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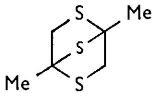
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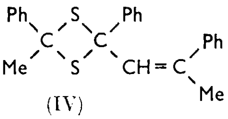
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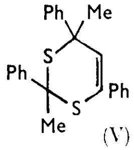
(V)

Only recently has it been possible by means of nuclear magnetic resonance spectroscopy to demonstrate with some certainty the 1,3-dithietan structure for some fluorinated thioketone dimers: perfluoro-2,4-di-n-butyl-2,4-dimethyl-1,3-dithietan[23] (I; $R^1 = R^3 = CF_3$, $R^2 = R^4 = [CF_2]_3{\cdot}CF_3$), perfluoro-2,2,4,4-tetramethyl-1,3-dithietan[24-26] (I; $R^1 = R^2 = R^3 = R^4 = CF_3$), perfluoro-2,2:4,4-bistrimethylene-1,3-dithietan[27] (I; $R^1R^2 = {\cdot}[CF_2]_3{\cdot}$; $R^3R^4 = {\cdot}[CF_2]_3{\cdot}$), and probably 2,4-diphenyl-2,4-bistrifluoromethyl-1,3-dithietan[28] (I; $R^1 = R^3 = Ph$; $R^2 = R^4 = CF_3$).

Methylene-1,3-dithietans are better known: the 2,4-dimethylene derivatives are known as desaurins,[29] and 2-dicyanomethylene-1,3-dithietan has recently been reported.[30]

We found that thiocyclohexanone[31] changed spontaneously to a crystalline solid, m. p. 132—133°, shown by analysis and molecular-weight determination to be a dimer. This dimer is quite resistant to alkali, and can be smoothly oxidised by potassium permanganate to a stable disulphone. The dimer could have had any of the structures (VI)—(IX), and it was hoped to synthesise these independently. *trans*-Cyclohexane-1,2-dithiol condensed smoothly with cyclohexanone in the presence of traces of a Lewis acid to yield compound (VII): Iqbal and Owen[32] obtained 2,2-dimethyl-*trans*-4,5-tetramethylene-1,3-dithiolan from *trans*-cyclohexane-1,2-dithiol and acetone in the presence of traces of sulphuric acid, and other similar dithiolans have been described.[33] However, synthesis of compounds (VI) and (IX) could not be achieved despite many attempts. [For compound (VIII), see later.]

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[14] K. Funck, Dissertation, Technische Universität, Berlin, 1954.

[15] E. Baumann and E. Fromm, *Ber.*, 1895, **28**, 895.

[16] D. J. Pasto and M. P. Servé, *J. Org. Chem.*, 1962, **27**, 4665.

[17] W. Ried and H. Klug, *Chem. Ber.*, 1961, **94**, 368.

[18] A. Behr, *Ber.*, 1872, **5**, 970.

[19] A. Schönberg and K.-H. Brosowski, *Chem. Ber.*, 1960, **93**, 2149.

[20] A. Schönberg, K.-H. Brosowski, and E. Singer, *Chem. Ber.*, 1962, **95**, 1910.

[21] E. Bergmann and J. Hervey, *Ber.*, 1929, **62**, 893.

[22] E. Campaigne and W. B. Reid, *J. Amer. Chem. Soc.*, 1946, **68**, 769.

[23] M. Hauptschein and M. Braid, *J. Amer. Chem. Soc.*, 1958, **80**, 853.

[24] E. G. Howard and W. J. Middleton, U.S.P. 2,970,173/1961 (*Chem. Abs.*, 1961, **55**, 14,311).

[25] W. J. Middleton, E. G. Howard, and W. H. Sharkey, *J. Amer. Chem. Soc.*, 1961, **83**, 2589.

[26] W. J. Middleton, U.S.P. 3,069,396/1962 (*Chem. Abs.*, 1963, **58**, 10,325); cf. K. V. Martin, *J.*, 1964, 2944.

[27] D. C. England, *Angew. Chem.*, 1962, **74**, 726.

[28] Th. J. Kealy, U.S.P. 3,069,397/1962 (*Chem. Abs.*, 1963, **59**, 1489).

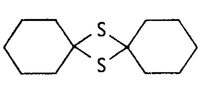
[29] P. Yates and D. R. Moore, *J. Amer. Chem. Soc.*, 1958, **80**, 5577, and references quoted therein; cf, A. Schönberg, E. Frese, and K.-H. Brosowski, *Chem. Ber.*, 1962, **95**, 3077.

[30] D. C. Dittmer, H. E. Simmons, and R. D. Vest, *J. Org. Chem.*, 1964, **29**, 497.

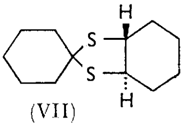
[31] R. Mayer, J. Morgenstern, and J. Fabian, *Angew. Chem.*, 1964, **76**, 157.

[32] S. M. Iqbal and L. N. Owen, *J.*, 1960, 1030.

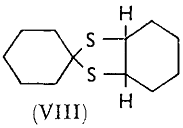
[33] C. C. J. Culvenor and W. Davies, *Austral. J. Sci. Res., Ser. A*, 1948, **1**, 236.



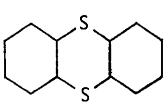
(VI)



(VII)

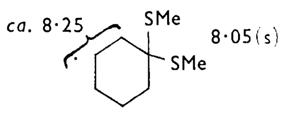


(VIII)



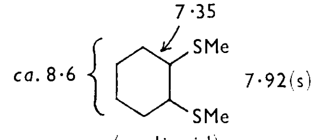
(IX)

The structure of the dimer was finally shown to be as (VI) by means of proton resonance spectroscopy. 1,1-Bismethylthiocyclohexane as (X)* was obtained from methanethiol and cyclohexanone (cf. ref. 34) and 1,2-bismethylthiocyclohexane (XI) by the alkylation of 2-methylthiocyclohexane-1-thiol with dimethyl sulphate. The corresponding disulphones (XII) and (XIII) were obtained by permanganate oxidation. Chemical shifts of the dimer, m. p. 132—133° (XIV), and its disulphone (XV), together with area measurements showed clearly the dithietan structure.



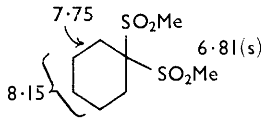
(as liquid)

(X)



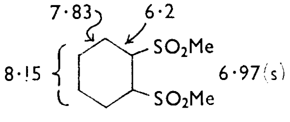
(as liquid)

(XI)



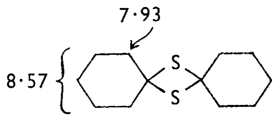
(in CHCl₃)

(XII)



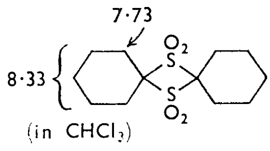
(in CHCl₃)

(XIII)



(in CCl₄)

(XIV)

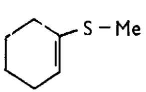


(in CHCl₃)

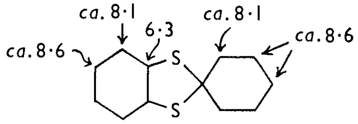
(XV)

The mechanism of 1,3-dithietan formation is not clear. Possibly the thioketone form of thiocyclohexanone, present in the nascent compound,[31] is involved. Radical initiators, such as azobisisobutyronitrile, apparently somewhat facilitate the dimerisation of thiocyclohexanone, and thus a radical process cannot be excluded.

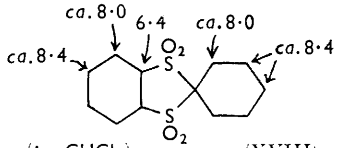
A second dimer, m. p. 59—61°, was obtained from thiocyclohexanone by treating an ethanolic solution of the thioketone, which had stood for some hours, with ethereal diazomethane. This unexpected result is in contrast with the reaction of thiocyclohexanone



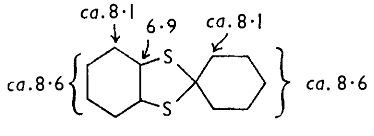
(XVI)



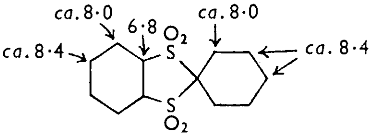
(in CCl₄) (XVII)



(in CHCl₃) (XVIII)



(in CCl₄) (XIX)



(XX)

(in dichlorotetrafluoroacetone deuterohydrate)

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* Chemical shifts for structure (X) and subsequent diagrams are shown in p.p.m. on the τ scale. All peaks were broad multiplets except those designated " s " which were singlets. Relative areas were in agreement with the assignments stated.

[34] A. C. Cope and Eu. Farkas, *J. Org. Chem.*, 1954, **19**, 385.

with diazomethane in absolute ether which yields 1-methylthiocyclohex-1-ene (XVI). The diazomethane evidently plays a catalytic role in dimer formation. Proton resonance spectroscopy shows that this dimer (XVII) and the corresponding disulphone (XVIII) have the dithiolan structure shown, and as it is different from the compounds (VII) synthesised as described above [for n.m.r. spectra see structure (XIX)], the dimer, m. p. 59—61°, is evidently 2,2-pentamethylene-*cis*-4,5-tetramethylene-1,3-dithiolan (VIII). A *cis*-1,3-dithiolan and a *cis*-trithiocarbonate were described[35] several years ago; the melting points of both compounds differed from those of the *trans*-isomers.[33,36] The disulphones (XVIII) and (XX) were obtained from the dithiolans by oxidation with peracetic acid.

EXPERIMENTAL

2,2:4,4-*Bispentamethylene*-1,3-*dithietan*.—(*a*) In the preparation of thiocyclohexanone according to ref. 37 (cf. also ref. 31), if the product is not cooled immediately to −70°, the deep red thioketone spontaneously decolourises with evolution of heat. The dimer slowly crystallises out of the oily product. After two days the whole is dissolved in hot acetone; cooling to 0° gives the *dimer* which after repeated recrystallisation from acetone or ethanol forms rhombs (13·3%), m. p. 132—133° [Found: C, 62·95; H, 8·8; S, 27·95%; *M* (cryoscopic in benzene), 233. $C_{12}H_{20}S_2$ requires C, 63·1; H, 8·85; S, 28·05%; *M*, 228].

(*b*) Freshly prepared thiocyclohexanone[37] (13·3 g.) was refluxed in carbon tetrachloride (50 c.c.) for 6 hr., when the original deep red colour paled to orange-red. After 12 hours' standing, the solvent was removed *in vacuo* and the residue taken up in acetone. On cooling, the dimer (1·4 g., 10·5%) separated, m. p. and mixed m. p. 131—133°.

(*c*) Addition of azobisisobutyronitrile (0·05 g.) to a reaction performed as in procedure (*b*) raised the yield to 20% and appeared to quicken the paling in colour.

2,2:4,4-*Bispentamethylene*-1,3-*dithietan* 1,1,3,3-*Tetroxide*.—Aqueous 5% potassium permanganate (66 c.c.) was added slowly with stirring to the dimer (1·8 g.); a permanent coloration just persisted at this point. More of this permanganate solution (33 c.c.) was then added. The whole was refluxed for 1 hr., cooled, and unreacted permanganate reduced with sodium hydrogen sulphite when the *disulphone* (1·8 g., 78%) separated; it formed sublimable rhombs (from ethanol), m. p. 259—260° [Found: C, 49·5; H, 6·95; S, 21·8%; *M* (Rast method in camphor), 352. $C_{12}H_{20}O_4S_2$ requires C, 49·3; H, 6·9; S, 21·95%; *M*, 292].

2,2-*Pentamethylene*-trans-4,5-*tetramethylene*-1,3-*dithiolan*.—Anhydrous zinc chloride (0·1 g.) was added to *trans*-cyclohexane-1,2-dithiol[38] (1 g.) and cyclohexanone (0·7 g.). The reaction mixture became warm and cloudy and, after 20 min., the product commenced to crystallise. After 24 hr. at 20°, the dithiolan (0·8 g., 52%) was recrystallised from methanol and ethanol to form compact prisms, m. p. 78—80° [Found: C, 63·1; H, 8·84; S, 27·95%; *M* (cryoscopic in benzene), 210].

2,2-*Pentamethylene*-cis-4,5-*tetramethylene*-1,3-*dithiolan*.—Freshly prepared thiocyclohexanone[37] (9·2 g.) was mixed with ethanol (50 c.c.). The solution, which lost its colour after 20 min., was set aside for 5 hr. at room temperature. Ethereal diazomethane was then added until a permanent yellow colour remained; when nitrogen evolution and spontaneous warming were marked, the reaction mixture was cooled. After 12 hr., solvents were distilled off and the residue was fractionated *in vacuo* to give some 1-methylthiocyclohexene (*ca.* 1 g.), b. p. 74—79°/14 mm., followed by the *dithiolan* (5 g.) as a light yellow oil, b. p. 162—165°/3 mm., which solidified and, after repeated crystallisation from methanol and ethanol, formed prisms (3 g., 32·6%), m. p. 59—61° [Found: C, 62·95; H, 8·85; S, 28·0%; *M* (cryoscopic in benzene), 226].

2,2-*Pentamethylene*-trans-4,5-*tetramethylene*-1,3-*dithiolan* 1,1,3,3,-*Tetroxide*.—The *trans*-dithiolan (1 g.) in acetic acid (50 c.c.) was allowed to react with aqueous hydrogen peroxide (100 vol.; 50 c.c.) for 4 days at 20°. The *disulphone* (0·9 g., 70%) separated; it was crystallised

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[35] L. Bateman, R. W. Glazebrook, C. G. Moore, M. Porter, G. W. Ross, and R. W. Saville, *J.*, 1958, 2838.

[36] C. C. J. Culvenor, W. Davies, and K. H. Pausacker, *J.*, 1946, 1050.

[37] R. Mayer and J. Jentzsch, *Angew. Chem.*, 1962, **74**, 292; *Angew. Chem. Internat. Ed.*, 1962, **1**, 217; R. Mayer and J. Jentzsch, *J. prakt. Chem.*, 1962, **18**, 211; J. Jentzsch, Dissertation, Technische Universität, Dresden, 1963.

[38] C. C. J. Culvenor, W. Davies, and N. S. Heath, *J.*, 1949, 282.

successively from nitromethane, benzene, ethyl methyl ketone, and benzene–ethanol (1 : 1) to form sublimable prisms, m. p. 250—258° [Found: C, 48·85; H, 6·95; S, 22·2%; *M* (isothermal distillation in chloroform), 285. $C_{12}H_{20}O_4S_2$ requires C, 49·3; H, 6·9; S, 21·95%; *M*, 292].

2,2-*Pentamethylene*-cis-4,5-*tetramethylene*-1,3-*dithiolan* 1,1,3,3-*Tetroxide* (78%) was similarly prepared; it separated from ethanol and acetone in needles, m. p. 200—203° [Found: C, 49·25; H, 6·95; S, 21·95%; *M* (isothermal distillation in acetone), 290].

1,1-*Bismethylthiocyclohexane.*—Dry hydrogen chloride and methanethiol were simultaneously led into cyclohexanone (50 g.) with cooling to below 0° for 3 hr. The mixture was then treated with water at 0°, the organic phase was taken up in light petroleum, repeatedly washed with aqueous sodium hydrogen carbonate and dried over sodium sulphate. Evaporation of the solvent gave the *thioketal* (73 g., 81%) as a colourless liquid, b. p. 70—72°/0·7—0·8 mm., n_D^{25} 1·5389 [Found: C, 54·95; H, 8·95; S, 36·45%; *M* (cryoscopic in benzene), 179. $C_8H_{16}S_2$ requires C, 54·5; H, 9·15; S, 36·35%; *M*, 176].

trans-1,2-*Bismethylthiocyclohexane.*—Potassium hydroxide (18·7 g.) in ethanol (100 c.c.) was saturated with methanethiol and then cyclohexene sulphide [39] (37·7 g.) added slowly with constant stirring and cooling to below 10°. After completion of the addition, stirring was continued for 5 hr. at 20° and the whole kept for 12 hr. Dimethyl sulphate (42 g.) was slowly added with stirring and cooling to below 40°. Ice–water (200 c.c.) and chloroform (100 c.c.) were added and the organic phase was washed repeatedly with water and dried (Na_2SO_4). Solvent was removed and the residue fractionated to yield the *cyclohexane* (19·5 g., 33·5%) as a colourless, strong-smelling liquid, b. p. 96—99°/1·7—2·0 mm., n_D^{20} 1·5440 [Found: C, 54·3; H, 9·35; S, 36·23%; *M* (cryoscopic in benzene), 186].

1,1-*Bismethylsulphonylcyclohexane.*—The thioketal (10 g.) in acetic acid (50 c.c.) was treated with 5% aqueous potassium permanganate, gradually at first, until a permanent colour persisted. The mixture was stirred for 5 hr. at 20° and the manganese dioxide filtered off (a small amount of disulphone was recovered by evaporation of the filtrate) and extracted repeatedly with hot methanol. The *disulphone* separated from the methanol as colourless crystals, m. p. 157—158° [Found: C, 40·35; H, 6·85; S, 26·6%; *M* (cryoscopic in benzene), 233, $C_8H_{16}O_4S_2$ requires C, 40·0; H, 6·7; S, 26·7%; *M*, 240].

1,2-*Bismethylsulphonylcyclohexane* (59%) was prepared similarly as colourless crystals, m. p. 170—172° [Found: C, 40·2; H, 7·02; S, 26·65%].

1-*Methylthiocyclohexene.*—Ethereal diazomethane was added to thiocyclohexanone (16 g.) in ether (50 c.c.) until a permanent yellow colour persisted. After the mixture had been left for 12 hr., the ether was removed and the residue fractionated to give the *sulphide* (9 g., 50%) as a mobile, evil-smelling liquid, b. p. 75·5—77°/16 mm., n_D^{20} 1·5252 [Found: C, 65·35; H, 9·75; S, 24·75%; *M* (cryoscopic in benzene), 118. $C_7H_{12}S$ requires C, 65·55; H, 9·45; S, 25·0%; *M*, 128].

Spectra were obtained at 40 Mc./sec. on a Perkin-Elmer nuclear magnetic resonance spectrometer with sample spinning. Tetramethylsilane was used as an internal reference. Concentrations were approximately 10% w/v.

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(A. R. K., M. J. S.) THE SCHOOL OF CHEMICAL SCIENCES, UNIVERSITY OF EAST ANGLIA,
NORWICH.
(R. M., J. M.) THE TECHNICAL UNIVERSITY,
DRESDEN, GERMANY.

[*Received, March* 10*th*, 1965.]

[39] *Org. Synth.*, 1952, **32**, 39.