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The Chemistry of Organic Compounds Containing the Thiodiimide Group

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Data on the methods of synthesis, the electronic and steric structures, and reactivities of organic compounds containing the thiodiimide group—N=S=N—are surveyed.
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I. INTRODUCTION

Heterocumulenes containing a quadrivalent dicoordinate sulphur atom are highly reactive and have unusual steric and electronic structures.[1] Among them, substances whose molecules incorporate the thiodiimide group −N=S=N−† are of special interest from both the theoretical and practical standpoints. Apart from the synthetic possibilities arising from these substances, the increased interest in them is associated with the fact that they can be regarded as the simplest oligomeric analogues of the polymeric sulphur nitride $(SN)_x$ [2]— a molecular metal and superconductor.[3,4] The informal character of the analogy is confirmed by the electrophysical properties of certain thiodiimides. In particular, poly(arylene thiodiimides) $(-Ar-N=S=N-)_n$ are semiconductors and exhibit photoconduction with a spectral sensitivity extending to the near infrared,[5,6] while a series of low-molecular-weight thiodiimides can be used as highly sensitive pigments in electrophotographic processes and in the generation of an image by means of photoelectrophoresis.[7]

The present review examines critically and gives a systematic account of the available information about the methods of synthesis, structure, and reactivity of open-chain compounds in which the thiodiimide group is linked to two organic or organoelemental moieties. Whenever possible, a comparison is made with the polymeric sulphur nitride $(SN)_x$. Heterocyclic compounds containing the −N=S=N− group, such as 2,1,3-thiadiazole and its derivatives, naphthol[1,8-*c*,*d*]-1,2,6-thiadiazine, etc., are not given special considerations. Studies on the coordination chemistry of organic thiodiimides, a review of which has been published recently,[8] are not examined either.

During the preparation of the review for the press, a survey of the chemistry of aza-analogues of sulphur dioxides, including thiodiimides, was published.[9] The present review was written from a somewhat different standpoint and is of a more specialist character, so that these two publications do not overlap but rather supplement one another.

†The −N=S=N− group does not have a generally accepted name in Soviet literature. We prefer to refer to it as the thiodiimide group following the authors of the following monograph: S.N.Borisov, M.G.Voronkov, and E.Lukevics, "Kremneorganicheskie Proizvoidnye Fosfora i Sery" (Organosilicon Derivatives of Phosphorus and Sulphur), Izd.Khimiya, Leningrad, 1968, p.202.

II. SYNTHESIS

Organic compounds containing the thiodiimide group can be synthesised from primary amines and elemental sulphur under conditions of the Pishchimuka reaction. However, this simplest reaction is one of the least investigated.

The most general method of synthesis of the compounds considered involves the interaction of primary amines with the halides of bivalent or quadrivalent sulphur or with *SS*-dihalogenosulphimines, which can be regarded as monoimino-derivatives of quadrivalent sulphur halides. Another general method of synthesis of thiodiimides involves the condensation of *N*-sulphinylamines or *N*-sulphinylamides. This procedure is partly related to the first group of reactions by the fact that *N*-sulphinylarylamines are the starting materials for the synthesis of *N*-aryl-*SS*-dichlorosulphimines.[10]

The third group of reactions, which lead to organic thiodiimides, are those of *NN*-dichloroamides with dichloromono- and dichlorodi-sulphanes, elemental sulphur, or *SS*-dichlorosulphimines, as well as the reactions of *N*-chlorobenzamides with sulphur. It may be[11,12] that these reactions proceed via the intermediate formation of thionitroso-compounds[13] or their dimers.

Sulphur nitride $(SN)_4$ and trithiazyl trichloride $(NSCl)_3$, whose synthetic possibilities have not apparently been as yet exhausted, serve as interesting sources of sulphur–nitrogen fragments for organic thiodiimides. The same compounds also function as starting materials in the synthesis of the polymeric sulphur nitrides $(SN)_x$.[3,4,14]

1. *NN*-Dialkylthiodiimides

NN'-Dialkylthiodiimides are obtained by the reaction of aliphatic amines with sulphur tetrahalides (or their monoimino-derivatives)[15-22] or with dichloromonosulphane.[18,23] They are also formed on thermolysis of *N*-thiosulphinyl-alkylamines[24] and on reaction of *N*-halogenoalkylamines with bis-(dimethylamino)-sulphane.[25] αα'-Bis(dialkylamino)-ααα'α'-tetrachloro-substituted thiodiimides are formed on interaction of cyanomides with dichloromonosulphane:[26]

$$AlkNH_2 \xrightarrow[-HX]{SX_4} AlkN{=}SX_2 \xrightarrow[-HX]{AlkNH_2} (AlkN{=})_2S;$$

$$AlkNH_2 \xrightarrow[-HX]{SCl_2} (AlkNS)_x \xrightarrow[-S]{\Delta} (AlkN{=})_2S;$$

X = Cl, F;

$$t\text{-}BuN{=}S{=}S \xrightarrow[-S]{\Delta} (t\text{-}BuN{=})_2S;$$

$$Alk_2N{-}CN \xrightarrow[-S_2Cl_2]{SCl_2} (Alk_2N{-}CCl_2{-}N{=})_2S\ .$$

Bis(perfluoroalkyl)thiodiimides have been synthesised from *SS*-dichloro-*N*-polyfluoroalkylsulphimines and trifluoromethylamine and its *NN*-dichloro-derivative.[27] In addition, *N*-heptafluoroisopropyl-*N'*-heptafluoroisopropylsulphenyl- and bis(heptafluoroisopropylsulphenyl)-thiodiimides are formed in low yields on interaction of thiazyl fluoride NSF with perfluoropropene.[28]

2. *NN'*-Bis(trimethylsilyl)thiodiimide and Related Compounds

NN'-Bis(trimethylsilyl)thiodiimide is formed on interaction of sodium *NN*-bis(trimethylsilyl)amide with thionyl chloride,[29] sulphur dioxide, or dichloromonosulphane[30] and also on interaction of trithiazyl trichloride with hexamethyldisilazane:[31]

$$\left.\begin{array}{l}(Me_3Si)_2NNa \xrightarrow{SOCl_2,\ SO_2\ \text{or}\ SCl_2} \\ (Me_3Si)_2NH \xrightarrow[-HCl]{(NSCl)_3}\end{array}\right\rangle \longrightarrow (Me_3SiN{=})_2S\,.$$

The reaction between trithiazyl trichloride and the corresponding tertiary amines is a more general process, which makes it possible to obtain bis(trimethylgermyl)- bis(trimethylstannyl)-, and bis(trimethylplumbyl)-thiodiimides in addition to the bis(trimethylsilyl) derivatives:[32]

$$(Me_3M)_3N \xrightarrow[-Me_3MCl]{(NSCl)_3} (Me_3MN{=})_2S\ ;$$
$$M = Si,\ Ge,\ Sn,\ Pb\,.$$

A group of monosilylated thiodiimides have been obtained by the single-stage reaction of *N*-sulphinylamines with lithium *NN*-bis(trimethylsilyl)amide,[33] while *N*-t-butyl-*N'*-trimethylsilylthiodiimide has been obtained by the reaction of *N*-sulphinyl-trimethylsilylamine with lithium t-butyldiorganylfluorosilylamides.[34] The latter substance has also been synthesised from *N*-t-butyl-*SS*-dichlorosulphimine and lithium *NN*-bis(trimethylsily)amide:[135]

$$(Me_3Si)_2NLi \left\langle \begin{array}{l} \xrightarrow{RNSO} R{-}N{=}S{=}N{-}SiMe_3\ ; \\ \xrightarrow[-LiCl;\ -Me_3SiCl]{t\text{-}BuN{=}SCl_2} t\text{-}Bu{-}N{=}S{=}N{-}SiMe_3\ ; \end{array}\right.$$
$$R = Et,\ t\text{-}Bu,\ Ph,$$
$$t\text{-}BuNLi \xrightarrow[-LiF;\ -1/n(-SiR_2O-)_n]{Me_3SiNSO} t\text{-}Bu{-}N{=}S{=}N{-}SiMe_3\,.$$
$$\quad |$$
$$\quad R_2SiF$$

N-Heptafluoroisopropyl-*N'*-trimethylsilylthiodiimide has been obtained from *N*-sulphinylheptafluoroisopropylamine and $(Me_3SiN{=})_2S$.[36]

A general procedure, consisting of the interaction of equimolar amounts of bis(trimethylsilyl)thiodiimide with arenesulphenyl chlorides, has been proposed for the synthesis of *N*-arenesulphenyl-*N'*-trimethylsilylthiodiimides:[2]

$$(Me_3SiN{=})_2S \xrightarrow[-Me_3SiCl]{ArSCl} Ar{-}S{-}N{=}S{=}N{-}SiMe_3\,.$$

N-Pentafluorobenzenesulphenyl-*N'*-trimethylsilylthiodiimide has been obtained from trithiazyl trichloride and *N*-pentafluorobenzenesulphenyl-*N*-trimethylsilylamine.[31]

Monosilylated thiodiimides are also formed in the reaction of sulphur nitride $(SN)_4$ with *N*-trimethylsilyl-substituted secondary alkylamines.[37] Bis(trimethylstannyl)thiodiimide has been synthesised by the reaction of $(SN)_4$ with *N*-trimethylstannyldimethylamine[38] or with tris(trimethylstannyl)amine:[39]

$$(SN)_4 \left\langle \begin{array}{l} \xrightarrow{(Me_3Sn)_3N\ \text{or}\ Me_2SnNMe_2} (Me_3SnN{=})_2S\ ; \\ \xrightarrow{Me_2SiNAlk_2} Me_3Si{-}N{=}S{=}N{-}S{-}NAlk_2\,. \end{array}\right.$$

3. *N*-Alkyl-*N'*-arylthiodiimides

N-Sulphenylaniline combines with lithium *N*-alkyl-*N*-trimethylsilylamides in petroleum ether. Subsequent reaction of the adducts with aluminium chlorides leads to *N*-alkyl-*N'*-phenylthiodiimides:[40]

$$\begin{array}{l} Alk \\ Me_3Si \end{array}\!\!>\!NLi \xrightarrow{Ph{-}NSO} \left[\begin{array}{l} Alk \\ Me_3Si \end{array}\!\!>\!N{-}SO{-}N\!<\!\begin{array}{l} Ph \\ Li \end{array}\right] \longrightarrow$$

$$\xrightarrow[-Al(OSiMe_3)_3]{AlCl_3} Ph{-}N{=}S{=}N{-}Alk\ ; \qquad Alk = Me,\ Et\,.$$

4. *NN'*-Diarylthiodiimides

The first diarylthiodiimides have been obtained by the condensation of *N*-sulphinylarylamines under the influence of metallic sodium.[41] *N*-Sulphinylaniline and its derivatives containing electron-donating substituents in the aromatic ring enter into this reaction. The yield of the products does not exceed 40%, which is probably associated with the elimination of sulphur from the thiodiimides on treatment with sodium to give azo-compounds. *N*-Sulphinylarylamines containing electron-accepting substituents do not undergo this reaction.[41]

N-Sulphinylarylamines also condense on treatment with alkali metal alkoxides, amides, and hydrides and dimsylsodium,[42–45] derivatives containing both electron-donating and electron-accepting groups in this ring undergoing the reaction. The most effective catalysts are alkali metal alkoxides and dimsylsodium. The yields of *NN'*-diarylthiodiimides are significantly higher than in the condensation of *N*-sulphinylamines under the influence of sodium.[42–45] The mechanism of the condensation of *N*-sulphinylarylamines on treatment with bases[43] is illustrated in Scheme (1) below

$$Ar{-}N{=}S{=}O \xrightarrow{B^-} \left[\begin{array}{l} Ar{-}\overline{N}{-}S{=}O \\ \qquad\quad | \\ \qquad\quad B \end{array}\right] \xrightarrow{Ar\text{-}NSO} \longrightarrow$$

$$\longrightarrow \left[\begin{array}{l} Ar{-}N{-}S{=}O \\ \qquad\quad |\ \diagdown B \\ \overline{O}{-}S{=}N{-}Ar \end{array}\right] \xrightarrow{-B^-} \qquad (1)$$

$$\rightarrow \left[\begin{array}{l} Ar{-}N{=}S{-}O \\ \qquad\quad |\ \ | \\ \qquad Ar{-}N{-}S{=}O \end{array}\right] \xrightarrow{-SO_2} (Ar{-}N{=})_2S\,.$$

It has been reported that the condensation of *N*-sulphinylaniline to give diphenylthiodiimide proceeds on treatment with zerovalent nickel complexes; however, the yields are low (12–20%). Substituted *N*-sulphinylanilines (4-Me-, 4-EtCO-) do not react.[46]

The most general method of synthesis of symmetrical diarylthiodiimides involves the interaction of arylamines with sulphur tetrafluoride.[47–50] Compared with other procedures, this method gives higher yields of purer products. Arylamines containing both electron-donating and electron-accepting groups,[48] including polyfluoroarylamines,[49,50] enter into this reaction. An essential condition is the removal of the hydrogen fluoride evolved during the reaction. Trimethyl- and triethyl-amines[47,48] as well as sodium fluoride[49,50] have been used as HF acceptors. In the first stage of the reaction the corresponding *N*-aryl-*SS*-difluorosulphimine is formed from the amine and sulphur tetrafluoride and then gives rise to the thiodiimide by reacting with a second arylamine molecule:

$$R{-}NH_2 \xrightarrow[-HF]{SF_4} R{-}N{=}SF_2 \xrightarrow[-HF]{R{\cdot}NH_2} (R{-}N{=})_2S\ ;$$
$$R = Ar,\ Ar_f\ .$$

The last reaction leads to a convenient procedure for the synthesis of asymmetric *NN'*-diarylthiodiimides. Its synthetic possibilities have been demonstrated in relation to the interaction of arylamines with *N*-aryl-*SS*-dichlorosulphimines,[10,51] *SS*-dichloro-*N*-pentafluorophenylsulphimine,[52,53] and *SS*-difluoro-*N*-polyfluoroarylsulphimines.[50,52] The reactions proceed smoothly and with satisfactory yields. Triethylamine, pyridine, and sodium fluoride have been used to combine with HCl and HF.[10,50-52]

The interaction of SF_4 with *N*-aryliminotriphenylphosphoranes also leads to the diarylthiodiimides. The reaction proceeds via the intermediate formation of *N*-aryl-*SS*-difluorosulphimines, which also makes it possible to obtain asymmetric derivatives:[54]

$$Ph_3P{=}NAr \xrightarrow[-Ph_3PF_2]{SF_4} Ar{-}N{=}SF_2 \xrightarrow[-Ph_3PF_2]{Ph_3P{=}NAr'} Ar{-}N{=}S{=}N{-}Ar'\ .$$

On treatment with sulphur tetrachloride, aniline is chlorinated in the ring and a thiodiimide is not then formed.[47] However, on reaction with dichlorodisulphane in the presence of pyridine, certain aromatic amines react to form *NN'*-diarylthiodiimides, the yields of the pure products exceeding 70%:[55]

$$Ar{-}NH_2 \xrightarrow[-HCl,\ -S]{S_2Cl_2} (Ar{-}N{=})_2S\ ;$$
$$Ar = 4\text{-}C_6H_4{-}N{=}N{-}C_6H_5,\ 4\text{-}ClC_6H_4,$$
$$4\text{-}EtOCOC_6H_4,\ 1\text{-naphthyl}.$$

The reactions of pentafluoroaniline[56] and 2,4-di(t-butyl)-6-methylaniline[1] with dichloromonosulphane also lead to the corresponding thiodiimides. The second product of the reaction of 2,4-di(t-butyl)-6-methylaniline with SCl_2 is 2,4-di(t-butyl)-6-methyl-*N*thiosulphinylaniline.[1] It is noteworthy that, on reaction with a large excess of dichloromonosulphane, arylamines form *N*-aryl-*SS*-dichlorosulphimines.[57]

A convenient preparative version of the synthesis of *NN'*-diarylthiodiimides using S_2Cl_2 and SCl_2 as sources of sulphur involves the interaction of the latter with aryl-*NN*-bis(trimethylsilyl)amines. *N*-Thiosulphinylanilines and thionitrosoarenes are probably formed as intermediates in these processes.[58]

It has been shown in relation to the 2,4-di(t-butyl)-6-methyl derivative that the photolysis of *N*-thiosulphinylanilines leads to diarylthiodiimides.[59] The thermolysis of 2,4-di(t-butyl)-6-methyl-*N*-thiosulphinylaniline in boiling benzene leads to the formation of benzoisothiazole and an arylamine,[59] while the thermolysis of 2,4,6-tribromo-*N*-thiosulphinylaniline affords the corresponding thiodiimide.[24]

Diarylthiodiimides have also been synthesised under the conditions of the Pishchimuka reaction[60] and on interaction of *SS*-dichloro-*N*-pentafluorophenyl-sulphamine with hexamethyldisilathiane:[24]

$$Ar{-}NH_2 \xrightarrow[Hg(HNAc)_2]{S_8} (Ar{-}N{=})_2S\ ;$$
$$Ph_f{-}N{=}SCl_2 \xrightarrow[-Me_3SiCl]{S(SiMe_3)_2} [Ph_f{-}N{=}S{=}S] \xrightarrow[-S]{} (Ph_f{-}N{=})_2S\ .$$

Yet another method leading to the synthesis of diarylthiodiimides involves the transamination of *NN'*-di(arenesulphonyl)thiodiimides. In the reaction of arylamines with *NN'*-di(benzenesulphonyl)thiodiimide in molar proportions of 1:1, one sulphonyl-amino-group is replaced by an arylimino-group and *N*-aryl-*N'*-benzenesulphonylthiodiimides are formed. When the latter are treated with aniline or arylamines containing electron-donating substituents in the ring, either the arylimino- or benzenesulphonyl group is displaced. If the arylimino-group contains no electron-accepting substituents, the benzenesulphonylimino-group is displaced and *NN'*-diarylthiodiimide is produced. Aromatic amines containing electron-accepting groups in the ring do not react with *N*-aryl-*N'*-benzenesulphonylthiodiimides. The diamides of *N*-arenesulphonylamino- or *N*-arylimino-sulphurous acids are apparently formed as intermediates in the transamination reaction of *NN'*-di(arenesulphonyl)thiodiimides:[61]

$$(PhSO_2N{=})_2S \xrightarrow[-PhSO_2NH_2]{ArNH_2} Ar{-}N{=}S{=}N{-}SO_2{-}Ph \xrightarrow[-PhSO_2NH_2]{Ar'NH_2}$$
$$\rightarrow Ar{-}N{=}S{=}N{-}Ar'\ .$$

5. *N*-Aryl-*N'*-arenesulphenylthiodiimides

N-Aryl-*N'*-arenesulphenylthiodiimides can be obtained by the reaction of the amides and imides of arenesulphenic acids with *N*-aryl-*SS*-dihalogenosulphimines and also with trithiazyl trichloride:[53]

$$Ph_f{-}S{-}NH_2 \xrightarrow[-HF]{Ph{-}N{=}SF_2} Ph_f{-}S{-}N{=}S{=}N{-}Ph\ ;$$
$$(PhS)_2NH \xrightarrow[-PhSCl,\ -HCl]{Ph_f{-}N{=}SCl_2} Ph{-}S{-}N{=}S{=}N{-}Ph_f\ ;$$
$$PhS{-}NH{-}Ph \xrightarrow[-HCl]{(NSCl)_3} Ph{-}S{-}N{=}S{=}N{-}Ph\ .$$

6. *N*-Aryl-*N'*-arenesulphonylthiodiimides

N-Aryl-*N'*-arenesulphonylthiodiimides can be obtained either by the transamination of bis(benzenesulphonyl)thiodiimides on treatment with an equimolar amount of an arylamine or by the reaction of *N*-arenesulphonyl-*SS*-dichlorosulphimines.[61,62] The only thiodiimide containing a heteryl substituent at the N=S=N group, namely *N*-benzenesulphonyl-*N'*-2-pyridylthiodiimide, has been obtained by the transamination of bis(benzenesulphonyl)thiodiimide with 2-aminopyridine and has been identified in the form of adducts with diene hydrocarbons.[63]

7. *NN'*-Di(arenesulphonyl)thiodiimides

When *NN*-dichloroamides of arenesulphonic acids are heated with sulphur in the absence of a solvent, chlorine is evolved and bis(arenesulphonyl)thiodiimides are produced in quantitative yields. It has been suggested that one of the intermediates in this reaction is the thio-analogue of a nitroso-compound, namely $Ar{-}SO_2{-}N{=}S$:[64]

$$Ar{-}SO_2{-}NCl_2 \xrightarrow[-Cl_2]{S} (Ar{-}SO_2{-}N{=})_2S \xleftarrow[-SO_2]{} O{=}S{=}N{-}SO_2{-}Ar\ .$$

However, heating of the *NN*-dichloroamides of pentafluorobenzene-sulphonic acid with sulphur affords the corresponding *SS*-dichlorosulphimine.[11]

The reactions of the *NN*-dichloroamides of arenesulphonic acids with sulphur chlorides and *N*-arenesulphonyl-*SS*-dichlorosulphimines, of arenesulphonamides[64] and hexamethyldisilathiane[24] with *N*-arenesulphonyl-*SS*-dichlorosulphonimines, and of *N*-arenesulphonyl-*SS*-bis(trimethylsilyl)sulphimines with dichloromonosulphane[24] also leads to bis(arenesulphonyl)-thiodiimides.

Another method of synthesis of bis(arenesulphonyl)thiodiimides involves the condensation of *N*-sulphinylarenesulphonamides. On treatment with $AlCl_3$ and tertiary amines, it occurs at 110–125 °C and at room temperature respectively, the yields of the bis(arenesulphonyl)thiodiimides being almost quantitative.[65]

Bis(benzenesulphonyl)thiodiimide has been obtained by heating *N*-sulphinylbenzenesulphonamide with *NN*-bis(trimethylsilyl)benzenesulphonamide:[66]

$$Ph{-}SO_2{-}NSO \xrightarrow[-(Me_3Si)_2O]{(Me_3Si)_2N{-}SO_2{-}Ph} (Ph{-}SO_2{-}N{=})_2S\ .$$

8. *N*-Arenesulphenyl-*N'*-arenesulphonylthiodiimides

N-Arenesulphenyl-*N'*-arenesulphonylthiodiimides are formed in low yields (5–7%) on reaction of trichloromethanesulphenyl chloride with the amides of arenesulphinic acids in boiling tetrachloroethylene. The main products of this reaction, whose mechanism is obscure, are diaryl disulphides and ammonium chloride:[67]

$$Ar{-}SO_2{-}NH_2 \xrightarrow[-(ArS)_2;\,-NH_4Cl]{Cl_3C{-}SCl} Ar{-}SO_2{-}N{=}S{=}N{-}S{-}Ar\ ;$$
$$Ar = Ph,\ Tol,\ 4\text{-}Cl{-}Ph\ .$$

N-Arenesulphinyl-*N'*-arenesulphonylthiodiimides have also been synthesised by the transamination of *NN'*-bis(arenesulphonyl)thiodiimides. For example, a mixed *N*-sulphenyl-*N'*-sulphonylthiodiimide is formed in satisfactory yield in boiling benzene from 2-nitrobenzenesulphenamide and ditosylthiodiimide; the reaction is catalysed by pyridine. In the presence of pyridine, the transamination of ditosylthiodiimide is also observed on treatment with *N*-sulphinylarenesulphenamides, but the yields are in this case only 10–17%. *N*-2-Nitrobenzenesulphenyl-*N'*-tosylthiodiimide has been synthesised from *SS*-dichloro-*N*-tosylsulphinamine and 2-nitrobenzenesulphenamide:[68]

$$(TosN{=})_2S \xrightarrow[-TosNX]{ArSNX} Tos{-}N{=}S{=}N{-}S{-}Ar \xleftarrow[-HCl]{ArSNH_2} TosN{=}SCl_2\ ;$$
$$X = H_2,\ SO;\ Ar = 2\text{-}O_2N{-}Ph\ .$$

9. *NN'*-Bis(arenesulphenyl)thiodiimides

The most general method of synthesis of bis(arenesulphenyl)thiodiimides involves the interaction of bis(trimethylsilyl)thiodiimide with arenesulphenyl chlorides.[2] This method makes it possible to obtain also asymmetric *NN'*-bis-(arenesulphenyl)thiodiimides by a two-stage reaction. In the reaction of bis(trimethylsilyl)thiodiimide with arenesulphenyl chloride in molar proportions of 1:1, the first stage involves the formation of *N*-arenesulphenyl-*N'*-trimethylsilylthiodiimide, which can be made to react with a secondary arenesulphenyl chloride molecule.[2]

$$(Me_3Si{-}N{=})_2S \xrightarrow[-Me_3SiCl]{ArSCl} Ar{-}S{-}N{=}S{=}N{-}SiMe_3 \xrightarrow[-Me_3SiCl]{Ar'SCl} \rightarrow Ar{-}S{-}N{=}S{=}N{-}S{-}Ar'.$$

Compounds containing a five-membered sulphur–nitrogen chain are also formed when sulphur nitride $(SN)_4$ reacts with diazo-compounds[7,69] and arylmagnesium bromides[70–72] but in the latter case the main products are diaryl disulphides:[71]

$$(SN)_4 \xrightarrow{ArMgBr} [(SN)_4\cdot 2ArMgBr] \xrightarrow{H_3O^+} (Ar{-}S{-}N{=})_2S;$$
$$(SN)_4 \xrightarrow[-N_2]{R_2CN_2} (R_2C{=}N{-}{-}N{=})_2S + R_2C\!\!<\!\!\begin{matrix}S\\ \\ \end{matrix}\!\!>\!\!CR_2\ .$$

Apart from the reactions listed above, several other processes leading to bis(arenesulphenyl)thiodiimides are known. Thus, when *N*-2-nitrobenzenesulphenyl-*N'*-tosylthiodiimide is refluxed in a mixture of benzene and morpholine (catalyst), it is symmetrised to form bis(2-nitrobenzenesulphenyl)thiodiimide. The same product has been obtained from *N*-2-nitrobenzenesulphenyl-*SS*-dichlorosulphimine and 3-nitroaniline and from 2-nitrobenzenesulphenamide and dichloromonosulphane.[68]

N-Benzenesulphenyl-*N'*-pentafluorobenzenesulphenylthiodiimide[53] and bis(pentafluorobenzenesulphenyl)thiodiimide[73] have been obtained by treating *N*-benzenesulphenyl-*N'*-pentafluorobenzenesulphenylamine and *NN*-bis(pentafluorobenzenesulphenyl)amine respectively with trithiazyl trichloride. Bis(pentafluorobenzenesulphenylthiodiimide) has also been obtained from SF_4 and pentafluorobenzenesulphenamide.[74] Bis(benzenesulphenyl)thiodiimide has been synthesised from thiodithiazyl dichloride $S_3N_2Cl_2$ and phenylmagnesium bromide.[72] The reaction of the tetrathiotetraimide $(SNH)_4$ with the corresponding arenesulphonyl chloride yielded bis(2,5-dichlorobenzenesulphenyl)- and bis(2,5-6-trichlorobenzenesulphenyl)-thiodiimides:[75]

$$(NSCl)_3 \xrightarrow[HCl]{RS{-}NH{-}SPh_f} R{-}S{-}N{=}S{=}N{-}S{-}Ph_f\ ;$$
$$R = Ph,\ Ph_f$$
$$(SNH)_4 \xrightarrow[-HCl;\,-SO_2]{ArSO_2Cl} (Ar{-}S{-}N{=})_2S\ .$$

10. *N*-Aryl-*N'*-phosphorylthiodiimides

Thiodiimides containing the phosphoryl group are formed when the *NN*-dichloroamides of dialkylphosphoric acids react with *SS*-dichlorosulphimines or hexamethyldisilathiane. It has been suggested that one of the intermediates in the latter reaction consists of thionitroso-compounds.[76] *N*-Phenyl-*N'*-(phenylphosphoramidyl)thiodimide has been obtained by the reaction of aniline with *SS*-dichloro-N-dichlorphosphorylsulphimine:[62]

$$(AlkO)_2P(O)NCl_2 \xrightarrow[-Cl_2]{Cl_2S{=}NR} (AlkO)_2P(O)N{=}S{=}NR\ ;$$
$$(AlkO)_2P(O)NCl_2 \xrightarrow[-Me_3SiCl]{S(SiMe_3)_2} [(AlkO)_2P(O)N{=}]_2S\ ;$$
$$R = Alk,\ SO_2Ar,\ P(O)(Alk)_2\ ;$$
$$Cl_2P(O)N{=}SCl_2 \xrightarrow[-HCl]{PhNH_2} Ph{-}N{=}S{=}N{-}P(O)(HNPh)_2.$$

11. *NN'*-Diaroylthiodiimides

Diaroylthiodiimides are produced (a) by the condensation of *N*-sulphinylbenzamides or by the reaction of benzamides with thionyl chloride, (b) by the reaction of *N*-chlorobenzamide with sulphur, and (c) by the reaction of *NN'*-diaroylamides of sulphoxylic acid with the *NN*-dichloroamides of sulphonic acids. All the reactions take place in the presence of pyridine. Dibenzoylthiodiimide has also been obtained by the reduction of methyl *N*-chloroiminobenzoate with sulphur or *N*-benzoyl-*SS*-dichlorosulphimine:[77,78]

$$ArCONH_2 \xrightarrow{SOCl_2} ArCO{-}NSO \xrightarrow{-SO_2}$$
$$ArCONHCl \xrightarrow{S}$$
$$(ArCONH_2)S \xrightarrow[-Ar'SO_2NH_2;\,-HCl]{Ar'SO_2NCl_2}$$
$$\Big\rangle\!\!\longrightarrow (ArCO{-}N{=})_2S;$$
$$PhC(OMe){=}NCl \xrightarrow[-MeCl \text{ or } -MeCl,\,-Cl_2]{S \text{ or } Cl_2S{=}N{-}COPh} (PhCO{-}N{=})_2S\ .$$

One of the mechanisms proposed for the interaction of *N*-chlorobenzamides with sulphur[77] involves the dehydrochlorination of *N*-chlorobenzamide with pyridine and the subsequent interaction of aroylnitrene with sulphur. The second mechanism proposed is illustrated schematically below:

$$ArCONCl \xrightarrow{S} ArCO{-}NH{-}SCl \xrightarrow[-Cl_2]{ArCONHCl} \rightarrow$$
$$\rightarrow (ArCONH)_2S \xrightarrow[-HCl]{Cl_2} (ArCO{-}N{=})_2S\ .$$

The interaction of the *NN*-dichloroamide of pentafluorobenzoic acid with sulphur leads to *SS*-dichloro-*N*-pentafluorobenzoylsulphimine.[11]

12. *NN'*-Bis(alkoxycarbonyl)thiodiimides

Bis(alkoxycarbonyl)thiodiimides have been synthesised from *NN*-dichlorourethanes on treatment with sulphur, dichloromonosulphane, or *N*-alkoxycarbonyl-*SS*-dichlorosulphimines. The reactions take place readily on heating the starting materials in the absence of a solvent and are accompanied by the evolution of chlorine:[79]

$$AlkO{-}CO{-}NCl_2 \xrightarrow[-Cl_2]{S,\ or\ SCl_2,\ or\ Cl_2S{=}N{-}COOAlk} (AlkOCO{-}N{=})_2S\ ;$$
Alk = Me, Et .

13. *N*-Alkyl(acyl)-*N'*-bromothiodiimides

N-Alkyl(acyl)-*SS*-dichlorosulphimines react with *N*-bromohexamethyldisilazane to form *N*-alkyl(acyl)-*N'*-bromothiodiimides:[80]

$$(Me_3Si)_2NBr \xrightarrow[-Me_3SiCl]{R{-}N{=}SCl_2} R{-}N{=}S{=}N{-}Br\ ;$$
$R = Alk_2C(CN),\ ArCO{-},\ ArSO_2{-}$

14. Compounds Containing More than One N=S=N Group in the Sulphur–Nitrogen Chain

When bis(trimethylsilyl)thiodiimide reacts with dichloromonosulphane in molar proportions of 2:1, 1,7,bis(trimethylsilyl)trithiotetranitride is formed, its sulphur–nitrogen chain consisting of two thiodiimide groups linked by a sulphide bridge.[81] The same substance has been obtained by the reaction of trithiazyl trichloride with hexamethyldisilazane.[31,82] 1,7-Bis(pentafluorophenyl) and 1,7-di-t-butyl-trithiotetranitrides have been synthesised from pentafluoro-*NN*-bis(trimethylstannyl)aniline and $S_3N_2Cl_2$ [83] or from *N*-t-butyl-*N'*-trimethylsilylthiodiimide and dichloromonosulphane[33,84] respectively:

$$\left.\begin{array}{l}(Me_3Si{-}N{=})_2S \xrightarrow[-Me_3SiCl]{SCl_2} \\ (Me_3Si)_2NH \xrightarrow[-HCl]{(NSCl)_3}\end{array}\right| \rightarrow (Me_3Si{-}N{=}S{=}N{-})_2S\ ;$$

$$Ph_f{-}N(SnMe_3)_2 \xrightarrow{S_3N_2Cl_2} (Ph_f{-}N{=}S{=}N{-})_2S\ ;$$

$$Me_3Si{-}N{=}S{=}N{-}Bu\text{-}t \xrightarrow[-Me_3SiCl]{SCl_2} (t\text{-}Bu{-}N{=}S{=}N{-})_2S$$

1,9-Diarylpentathiotetranitrides,[2] compounds which are known at present to have the longest (for non-polymeric molecules) sulphur–nitrogen chains, are obtained by the reaction of *N*-2-nitrobenzenesulphenyl- and *N*-2,4-dinitrobenzenesulphenyl-*N'*-trimethylsilylthiodiimides with dichloromonosulphane:

$$Ar{-}S{-}N{=}S{=}N{-}SiMe_3 \xrightarrow[-Me_3SiCl]{SCl_2} (Ar{-}S{-}N{=}S{=}N{-})_2S\ .$$

When an attempt was made to obtain an even longer sulphur–nitrogen chain by the reaction of dichloromonosulphane with 1,7-bis(trimethylsilyl)trithiotetranitride, only sulphur nitride $(SN)_4$ was obtained.[81]

15. Poly(arylenethiodiimides)

The condensation of aromatic *NN'*-disulphinyldiamines catalysed by potassium or lithium t-butoxides leads to poly(arylenethiodiimides). Polymers with *p*-phenylene units in the chain are almost insoluble in organic solvent. The derivatives containing *m*-aniline units are soluble in some cases; they are apparently macrocyclic. The determination of the molecular weight of a soluble polymer obtained from bis(3-*N*-sulphinylamino-4-methoxyphenyl)methane yielded a value corresponding to the octamer.[5,6]

Poly(arylenethionitrides) have been obtained from sulphur nitride $(SN)_4$ and phenylenebisdiazoalkanes.[85] The determination of the molecular weight of one of them (R = Ph, Ar = C_6H_4) showed that it is a trimer:

$$RC{-}Ar{-}CR \xrightarrow[-N_2]{(SN)_4} \longrightarrow (-Ar{-}C{=}N{-}S{-}N{=}S{=}N{-}S{-}N{=}C{-}Ar{-}C{-}C{-})_n$$
(R: on the C=N carbon; R R: on the C–C carbon)

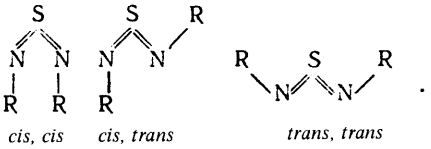
III. GEOMETRY AND ELECTRONIC STRUCTURE

Dialkyl-, diaryl-, and bis(arenesulphonyl)-thiodiimides exist predominantly in the form of *cis,trans*-isomers with a small admixture (in solution) of *trans,trans*-isomers. When a longer sulphur-nitrogen chain is incorporated in the composition of the compound, the thiodiimide group is retained as an independent structural unit, but the molecules of bis(arenesulphenyl)thiodiimides now have the *cis,cis*-geometry. Five-membered sulphur–nitrogen chains in organic derivatives are just as planar as the "infinite" $(SN)_x$ macromolecules.

The electronic structure of the thiodiimide group in organic derivatives is extremely sensitive to the influence of substituents and is capable of undergoing a significant rearrangement under their influence. In aromatic derivatives the thiodiimide group conjugated with organic fragments is a weak electron donor and transmits the electronic effects of substituents. At the same time many important details of the electronic structure of the organic thiodiimides remain obscure and require further study.

1. The Geometry of the Molecules of Organic Thiodiimides

Theoretically, organic thiodiimides can exist in the form of three geometrical isomers:



According to electron diffraction[86] and X-ray diffraction[86,87] data, the molecules of dimethylthiodiimides in the gas phase and of di-*p*-tolyl- and ditosyl-thiodiimides in the crystalline form have the *cis,trans*-configuration, the bond lengths and valence angles of which are given in Table 1. The lengths of the SN bonds in the thiodiimides are significantly closer to

the value for the sulphur–nitrogen double bond (1.52 Å) than for the single bond (1.74 Å). The distance between the nitrogen atoms rules out a valence interaction between them.[87]

Table 1. Parameters of the molecules of certain organic thiodiimides R–N=S=N–R.*

R	Bond lengths, Å				Valence angles, deg		
	SN_{cis}	SN_{trans}	NR_{cis}	NR_{trans}	RNS_{cis}	RNS_{trans}	NSN
Tol	1.53	1.56	1.46	1.41	131	118	117
Tos	1.52	1.52	1.68	1.69	125	117	115
Me	1.53	1.53	1.46	1.46	125	117	114

*According to the data of Kuyper et al.[86] and Leandri et al.[87]

The carbon, nitrogen, and sulphur atoms in the molecule of dimethylthiodiimide lie in the same place.[86] However, analysis of the vibrational spectra of bis(trimethylsilyl)thiodiimide led Herbrechtshmeier et al.[88] to the conclusion that the planar conformation of the $(SiN=)_2S$ fragment with C_{2v} or C_s point symmetry is ruled out and that a non-planar conformation with C_2 point symmetry is most probable.[88]

There is a deviation from planarity also in the molecule of di-*p*-tolyl-thiodiimide: in the crystalline state the planes of the aromatic rings form dihedral angles of 21.9° and 39.9° with the plane of the NSN atoms;[87] it may be that this is associated in the first place with the characteristic features of the crystal packing.

In solution dialkyl-[22,89] and diaryl-thiodiimides[48] exist in the form of an equilibrium mixture of the *cis,trans*- and *trans,trans*-isomers according to ^{13}C and ^1H NMR, the former isomer being always present in a greater amount. In the case of the dimesitylthiodiimide, only the *trans,trans*-isomer is present for steric reasons.[48] The activation energy for the interconversion of the isomers of diarylthiodiimide is in the range 11–12 kcal mol^{-1} and the frequency factor is approximately 10^{13} s^{-1}, which is usual for unimolecular reactions with an unstrained transition state. The electron-donating groups in the 4,4′-positions in the aromatic rings diminish the rate of interconversion of the isomer. The rates of the interconversions of the isomers of dialkylthiodiimides are lower than those for the diaryl derivatives.[22,48]

The increase in the length of the sulphur–nitrogen chain on passing from diaryl- to bis(arenesulphenyl)-thiodiimides is accompanied by changes in molecular geometry. According to X-ray diffraction data, the arenesulphenyl fragments in the molecules of bis(benzenesulphenyl)thiodiimide[90] and bis-(4-chlorobenzenesulphenyl)thiodiimide[91] are located in the *cis,cis*-positions relative to the central N=S=N unit. The distances between the nitrogen atoms and the central sulphur atom typical for SN double bonds agree well with the values found for di-*p*-tolylthiodiimide (Table 1). The distances between the nitrogen atoms and the sulphur atoms at the edges (1.66 Å) have the usual values for SN single bonds, in which there is the possibility of some d_π–p_π overlap.[91] The distance between the extreme sulphur atoms (3.29 Å) greatly exceeds the length of the covalent SS bond, but is somewhat smaller than the sum of the van der Waals radii of two sulphur atoms, which may indicate a weak interaction. The valence angle at the central sulphur atom is 124° and those at the nitrogen atoms are 129° and 126°.[91]

The most characteristic features of the steric structure of the bis(4-chlorobenzenesulphenyl)thiodiimide molecule is its close approximation to planarity (a single plane with an average deviation of the atoms of 0.11 Å and a maximum deviation of 0.24 Å can be adopted for the entire molecule) and the virtual collinearity of the axes of the aromatic rings (the projections of the lines passing through the Cl and S atoms in each of the 4-chlorobenzenesulphenyl groups onto the plane of the molecule form an angle of 190°).[91] However, the benzene rings in the bis(benzenesulphenyl)thiodiimide molecule have been rotated by 30.8° relative to the average plane of the nitrogen and sulphur atoms.[90]

The latest of the open-chain thiodiimides whose real geometry is known is 1,5-bis(diphenylmethyleneimino)trithiodinitride $Ph_2C=N-S-N=S=N-S-N=CPh_2$. The central sulphur atom of the molecule is located on a twofold symmetry axis; the valence angle at this atom is 124°. The substituents are located in the *cis,cis*-positions relative to the central N=S=N unit. The five central atoms of the sulphur–nitrogen chain are located in the same plane (with deviations within the limits of 0.04 Å), while the remaining two nitrogen atoms deviate from this plane by 0.49 Å. The SN bond lengths in the =S=N–S–N= fragment are respectively 1.55, 1.66, and 1.69 Å; the valence angles at the nitrogen atoms of the central N=S=N unit are 126°.[92,93]

It is of interest to compare the geometry of the molecules of organic thiodiimides with the geometry of the macromolecules of the polymeric sulphur nitride $(SN)_x$, which consist of chains of alternating sulphur and nitrogen atoms.[3,4] If one isolates an arbitrary NSN fragment in the $(SN)_x$ macromolecule, then the chain is continued in the *cis,trans*-positions, in a manner resembling the disposition of the substituents in the *cis,trans*-positions relative to the thiodiimide group in dialkyl, diaryl, and bis(arenesulphonyl) derivatives. However, the SN bond lengths in $(SN)_x$, which alternate (1.63 and 1.59 Å), appreciably exceed those in the thiodiimide group. The valence angles at the sulphur atoms in the $(SN)_x$ molecule are 106°, which is much less than the angle at the sulphur atom of the thiodiimide group. The valence angles at the nitrogen atoms (120°) are somewhat greater than the angles at the nitrogen atom of the N=S=N group linked to a *trans*-substituent, but are smaller than at the nitrogen atom linked to a *cis*-substituent.

2. The Electronic Structure of the Molecules of Organic Thiodiimides

(a) Electronic spectroscopic data and the results of quantum-chemical calculations. According to the data of Schouten and Oskam[94] and Kroner et al.,[95] the He(I) photoelectron spectra of dialkylthiodiimides contain three distinct peaks separated from a series of poorly resolved bands (with the exception of the spectrum of the diethyl derivative in which five peaks are resolved[94]). The interpretation of the spectra in terms of the Koopmans theorem on the basis of the quantum-chemical calculation by the LCAO-MO SCO method in terms of the CNDO/2 valence approximation, including the 3*d* AO of sulphur in the basis set, showed[94] that the first ionisation potential (IP) corresponds to the removal of an electron from the π MO made up of the d_{yz} AO of sulphur and the p_z AO of nitrogen. The next two bands correspond to the ionisation of orbitals of the σ type, the first of which constitutes a symmetrical combination of the AO ("unshared pairs") of nitrogen and sulphur and the second an antisymmetric combination of the AO ("unshared pairs") of nitrogen without the participation of the AO of sulphur. The fourth

band (usually a shoulder against the background of the ionisation of the σ skeleton) corresponds to the ionisation of the π MO made up of the p_z AO of nitrogen and sulphur. Comparison of the results of calculations by the CNDO/2 method for the *cis,trans*- and *trans,trans*-isomers of dimethylthiodiimides shows certain differences between the one-electron MO energies while their sequence is the same.[94] The MO in Table 2, which summarises the photoelectron spectroscopic data for dialkylthiodiimides, are therefore classified in terms of the irreducible representations of the symmetry point group C_{2v} of *trans,trans*-dimethylthiodiimide.

Table 2. The vertical ionisation potentials (IP) and one-electron MO energies of dialkylthiodiimides (AlkN=)$_2$S.*

IP, eV				One-electron MO energies**, eV (Alk = Me)		Assignment*
Me	Et	iso-Pr	t-Bu	*cis, trans*	*trans, trans*	
9.16	8.90	8.75	8.61 (8,65)	12.37	12.25	a_2 (a_2)
9.86	9.62	9.43	9.06 (9,01)	13.37	13.03	a_1 (a_1)
10.55	10.26	10.05	9.57 (9,60)	13.58	14.15	b_1 (b_2)
11.91	11.62	11.34	11.10 (11,1)	14.81	14.90	b_2 (b_1)
12.85	12.2	11.7	11.6	16.45	16.84	b_1

*According to the data of Schouten and Oskam[94] (the data of Kroner et al.[95] are given in brackets).
**Quoted with the sign reversed.

The substitution of the alkyl groups by trimethylsilyl groups alters the sequence of the MO. Interpretation of the He(I) photoelectron spectrum of bis(trimethylsilyl)-thiodiimide on the basis of the quantum-chemical calculations in terms of the MINDO approximation using the Koopmans theorem showed that the first three vertical IP (IP_1 = 9.2 EV) correspond to the MO with a predominant contribution by the AO of nitrogen: the non-bonding $a_2(\pi)$ MO made up of the p_z AO of nitrogen and the antisymmetric (b_2) and symmetrical (a_1) combinations of the AO of the "unshared pairs" of nitrogen.[96]

However, one should note that the interpretation of the photoelectron spectra on the basis of theoretical calculations alone, which are usually semiempirical, is not reliable and must be treated with caution. Calculations in terms of the CNDO approximation frequently yield an incorrect sequence of the orbitals, in particular certain σ MO are placed above the π MO.[97]

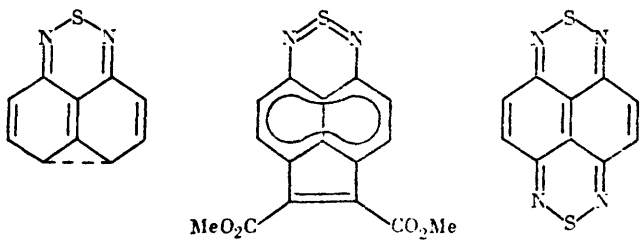
An increase in the length of the sulphur–nitrogen chain entails a decrease of the first IP. Thus IP_1 = 7.85 eV for 1,7-bis(trimethylsilyl)trithiotetranitride.[96]

Organic thiodiimides containing aromatic substituents have not been investigated by photoelectron spectroscopy with the exception of naphtho[1,8-*cd*]-1,2,6-thiadiazine, whose He(I) spectrum proved to be similar to that of 2-methyl-naphtho-[1,8,*de*]-1,2,6-triazine. A great similarity has also been observed between the electronic absorption spectra. The interpretation of the spectra based on calculations by the extended Hückel method and in terms of the MINDO/3 approximation has been carried out on the assumption that the bands in the electronic absorption spectra are associated with $\pi \rightarrow \pi^*$ transitions and that the Koopmans theorem holds for the photoelectron spectra; this interpretation showed the observed similarity between the spectra is due to the similarity between the structures of the valence levels. Thus it follows that, in considering the thiodiimide group, one can neglect the structure with quadrivalent sulphur (–N=S=N–) and the group can be described in terms of the superposition of structures of type (2). In terms of the LCAO-MO theory, this means that the 3*d* AO of sulphur are unimportant for the ground and excited states of the thiodiimide group:[98]

$$R-\bar{N}-\overset{+}{S}=N-R \longleftrightarrow R-N=\overset{+}{S}-\bar{N}-R \,. \qquad (2)$$

However, one can adduce certain considerations in support of the view that the conclusions valid for a system such as naphtho[1,8-*cd*]-1,2,6-thiadiazine can be hardly extended to derivatives of an organic compound with the thiodiimide group, at any rate without special stipulations.

In the first place, one should note that the 3*d* AO of sulphur, which appear in semiempirical quantum-chemical calculations, are usually no more than correction functions applied to an incorrect basis set, which are of purely methodological importance,[99] and the results of such calculations cannot serve as reliable arguments in the solution of the problem of the involvement or non-involvement of the 3*d* AO of sulphur in the formation of a chemical bond. The 3*d* AO of sulphur are capable of participating effectively in the formation of a chemical bond only when there is a large positive charge on the sulphur atom. The population of the 3*d* AO is usually small and their role consists of not so much in increasing the strength of the bonds as in converting the non-bonding MO into bonding MO and in decreasing the anti-bonding character of the antibonding MO.[100] The charge on the sulphur atom of naphtho[1,8,-*cd*]-1,2,6-thiadiazine is unknown, but in certain thiodiimides (see below) it is sufficiently high to permit the involvement of the 3*d* AO of sulphur in bonding. Furthermore, naphtho[1,8-*cd*]-1,2,6-thiadiazine has a number of features which distinguish it from open-chain thiodiimides. In particular, one can consider the quinonoid structures (A) for this compound with a formal π-bond between the carbon atoms in the 4- and 5-positions, which agrees with the fact that it reacts with bis-(methoxycarbonyl)acetylene to form the acenaphthothiadiazine (B) via [12π + 2π]-cycloaddition and aromatisation.[101] The position of the ^{15}N NMR signal of naphtho[1,8-*cd*]1,2,6-thiadiazine in a weaker field compared with that of diphenyl-thiodiimide can be accounted for[102] by the contribution of this structure. Naphtho[1,8-*cd* : 4,5-*c'd'*]bis-1,2,6-thiadiazine, which is a very close analogue of naphtho[1,8-*cd*]-1,2,6-thiadiazine, is a weakly aromatic compound and its structure (C) probably contributes to its ground state.[103]



(A) (B) (C)

Organic compounds containing the thiodiimide group have not been investigated systematically by X-ray electronic spectroscopy. The determination of the bond energies E_b of the internal levels of the nitrogen and sulphur atoms in di-t-butylthiodiimide [$E_b(S_{2p_{3/2}})$ = 166.9 eV; $E_b(N_{1s})$ = 398.4 eV] [95] and bis(trimethylsilyl)thiodiimide [$E_b(S_{2p})$ = 164.9 eV; $E_b(N_{1s})$ = 397.5 eV] [81] showed that the E_b for the N_{1s} level and hence the effective charge on the nitrogen atom can change significantly as a function of the substituents to

which the N=S=N group is linked.# This agrees with the results of measurements of the effective charges on the sulphur atoms in organic thiodiimides by X-ray fluorescence spectroscopy. The positive charges within the volume defined by the covalent radius, determined from the shifts of the S K_α lines, vary within the following ranges (in units of the electronic charge): 0.28–0.33 for diarylthiodiimides, 0.24–0.36 for *N*-aryl-*N'*-polyfluoroarylthiodiimides, and 0.25–0.35 for bis(polyfluoroaryl)thiodiimides.[50] The charge on the sulphur atom in these compounds exceeds that in bis(pentafluorophenyl)disulphide, the X-ray spectroscopic study of which (S $L_{II,III}$ spectrum) showed that the 3*d* AO of sulphur are not involved in the formation of the chemical bond in this compound.[105] Thus the charges on the sulphur atom in the thiodiimide group linked to aryl and (or) polyfluoroaryl substituents do not rule out the possibility of the involvement of the 3*d* AO of sulphur in chemical bonding.

The distribution of the 3*p* electrons of the sulphur atoms among the MO in diarylthiodiimides and *N*-aryl-*N'*-polyfluoroarylthiodiimides (according to S K_β spectra) resembles that in aromatic sulphides. On passing to bis(polyfluoroaryl)thiodiimides, the character of the distribution of the 3*p* electrons of sulphur among the MO changes sharply and becomes similar to the distribution of the 3*p* electrons of sulphur among the MO in SO_2.[50] This result has been interpreted[50] as a consequence of the significant weakening of the effectiveness of the p_π–p_π interaction between the heteroatom and the polyfluoroaryl group linked to it compared with the aryl group;[106] this shows that the electronic structure of the thiodiimide group is extremely sensitive to the influences of the substituents and can undergo an appreciable rearrangement under such influence. An alternative explanation consists in a possible increase of symmetry from C_s to C_{2v} on passing from diaryl- to bis(polyfluoroaryl)-thiodiimides (i.e. on passing from the *cis,trans*-configuration to the *trans,trans*-configuration), but direct structural information does not exist.

The agreement between the effective charges on the sulphur atoms in the molecules of bis(4-methyl-2,3,5,6-tetrafluorophenyl)thiodiimides[50] and the polymeric sulphur nitride $(SN)_x$ [107] molecules makes it possible to compare[108] the S K_β spectra of these compounds directly in terms of the scale of the transition energies. The comparison shows that, in the short-wavelength region (~2468–2473 eV), where transitions from the π^* antibonding and π bonding MO are manifested in the S K_β spectrum of the sulphur nitride $(SN)_x$,[107] the spectra are similar as regards the form of the spectral line and the energies of its structural elements. From this it follows that populated π^* MO, antibonding in sulphur–nitrogen bonds, exist in bis(polyfluoroaryl)thiodiimides.

Calculations of the MO of dimethylthiodiimide in terms of the CNDO/2 approximation taking into account the 3*d* AO of sulphur showed[94] that the π^* antibonding MO in this molecule is unoccupied, being only virtual (LUMO). The antibonding π^* MO in the ground state can be populated only as a result of the interaction of the group π orbitals of the NSN fragment with the group π orbitals of the aromatic rings. The existence of the π interaction of the NSN group with aromatic substituents is also indicated by the changes in the relative intensities and width of the bands in the S K_β spectra of thiodiimides with aromatic (including polyfluorinated) substituents when the groups in the 4,4'-positions in the rings are varied.[50] This interaction leads to the existence of a series of many-centre MO, embracing both the NSN fragment and the aromatic rings, i.e. to the delocalisation of the π bonding throughout the molecule, which is outwardly expressed by the ability of the thiodiimide group to transmit the electronic influences of the substituents. A study of the ^{19}F NMR spectra of the compounds C_6F_5–N=S=N–C_6H_4–X-4 showed[50] that the relative chemical shift (relative to X = H) of the signal of the *p*-fluorine atom in the pentafluorophenyl ring is satisfactorily correlated with the Hammett σ_p constant of the substituent X.

In the electronic spectra of the organic thiodiimides R–N=S=N–R the long-wavelength absorption maximum undergoes a bathochromic shift on passing from alkyl or acyl derivatives (R = alkyl, AlkOCO, or $ArSO_2$) to monoaryl and further to diaryl derivatives.[51] In a series of symmetrical diarylthiodiimides both electron donating and electron accepting substituents in the 4,4'-positions in the rings induce a bathochromic shift of the long-wavelength absorption maximum[51] (Table 3). The characteristic long-wavelength absorption bands of symmetrical diarylthiodiimides are almost insensitive to the influence of solvents, while symmetrical derivatives of the type 4-$O_2NC_6H_4N$=S=NC_6H_4X-4 and $C_6H_5SO_2N$=S=NC_6H_4X-4 exhibit negative solvatochromism.[51] The long-wavelength absorption band in the electronic spectra of compounds of the latter two types is extremely sensitive also to the character of the substituents in the aromatic rings.[109] Electron-donating substituents X shift the absorption maximum towards longer wavelengths and the magnitude of the shift of λ_{max} (relative to the λ_{max} of the analogous compound with X=H) is satisfactorily correlated with the Hammett or Taft constant for the majority of substituents X. Electron-accepting substituents X hardly influence the position of the maximum or shift it towards shorter wavelengths. On the basis of the facts described, it has been concluded[109] that the band considered is apparently associated with the electron transfer not through the entire π system of the molecule but mainly through the unoccupied 3*d* AO of the sulphur.

Table 3. The long-wavelength absorption maxima in the electronic spectra of certain organic thiodiimide R–N=S=N–R.

R	λ_{max}, nm (lg ϵ)	Solvent	Refs.
t-Bu	276	*	[92]
Me_3Si	273 (~4)	Chloroform	[2]
Me_3Si	271.5	*	[92]
Ph	410 (3.98)	Ethanol	[47]
Ph	418	Ethanol	[51]
Ph	420 (4.07)	Benzene	[51]
4-$O_2NC_6H_4$	431 (4.26)	Benzene	[51]
4-$Me_2NC_6H_4$	532 (4.50)	Benzene	[51]
C_6F_5	390	Hexane	[49]
PhS	452	Dioxan	[85]
PhS	446	Acetonitrile	[72]
Ph_2C=NS	508	Benzene	[69]

*In the gas phase.

An increase in the length of the sulphur–nitrogen chain is accompanied by a bathochromic shift of the long-wavelength of the absorption maximum, which has been interpreted[2] as a consequence of the increase of the electron delocalisation along the chain. λ_{max} of the long-wavelength band varies

#Provided that this result is not associated with an error in calibration. The spectrum has been calibrated[95] in accordance with the exact value $E_b(C_{1s})$ = 285.0 eV;[104] Lidy et al[81] could not deal with this question in detail. According to Lindberg and Hedman,[104] the absolute values of E_b quoted in the early studies, based on a calibration in terms of the C_{1s} line, must be increased by 1 eV. If this applies to the study of Lidy et al,[81] then the E_b for the N_{1s} level in the compounds under discussion are virtually identical.

in the range 382–413 nm for the compounds $ArSN{=}S{=}NSiMe_3$, 448–476 nm for $(ArSN{=})_2S$, and 580–587 nm for $(ArSN{=}S{=}N)_2S$. Since electron-accepting substituents in aryl rings increase slightly the bathochromic shift, the delocalisation of the π bonding apparently embraces also the aromatic rings.[2]

Theoretical interpretation of the electronic absorption spectrum of diphenylthiodiimide on the basis of the p_π model of sulphur shows that the properties of this and similar compounds described here are associated with the presence of the quasi-polymethine chromophore NSN and the idea that the 3*d* AO of sulphur are involved is not essential for their understanding.[110] The long-wavelength absorption band is associated with the $\pi \rightarrow \pi^*$ transitions. The first excited state of diphenylthiodiimide can be described, in terms of the "molecules in the molecule" method, by a superposition of the locally excited (LE) configuration of the thiodiimide group and the configuration with charge transfer (CT) from the N=S=N fragment to the phenyl group. Comparison of the calculated spectroscopic characteristics of diphenylthiodiimide and the hypothetical *N*-hydro-*N'*-phenylthiodiimides indicates the importance of the presence of two phenyl substituents in the molecule of the former compound. The study of the interaction between the LE configuration of the N=S=N group and the N=S=N–phenyl CT configuration showed that the energy level of the first excited state is split by the CT configuration with participation of the second benzene ring.[110]

The energies of the $\pi \rightarrow \pi^*$ transitions in dimethylthiodiimides, benzo-2,1,3-thiadiazole, and naphtho[1,8-*cd*]-1,2,6-thiadiazine, evaluated from the results of the calculation by the CNDO/2 method using the virtual orbital approximations for the excited states, agree directly with experiments. The inclusion of the 3*d* AO of sulphur in the basis set lowers the HOMO energy, which increases the energy of the electronic transition and impairs the agreement between the theoretical and experimental values.[111]

For organic compounds containing the thiodiimide group, non-empirical quantum-chemical calculations have not been made. According to a calculation by the CNDO/2 method with inclusion of the 3*d* AO of sulphur in the basis set, the sulphur atom in dimethylthiodiimide has an effective positive charge of 0.21 e, induced, according to the analysis of the orbital populations, by the SN π-bond.[94] According to Grunwell and Danison,[112] in the CNDO/2 calculations for *NN'*-dimethylthiodiimide and the hypothetical *NN'*-dihydrothiodiimide, the effect of the inclusion of the 3*d* AO of sulphur in the basis set is expressed predominantly by the achievement of a satisfactory agreement between the SN bond lengths and the experimental values and by the stabilisation of the planar conformation via the so-called π' bonding. The inclusion of the 3*d* AO of sulphur does not influence the symmetries of the HOMO and the LUMO, but the geometrical isomerism does affect the symmetry of the HOMO.[113]

According to a calculation in terms of the CNDO/2 approximation, without taking into account the 3*d* AO of sulphur,[110] the distribution of electron density within the limits of the NSN fragment of diphenylthiodiimide is ylide-like but with a considerable amount of SN double bond character, which can be reproduced by a superposition of structures (2) while the valence state of the sulphur atom is intermediate between its state in the thiocarbonyl group and in the thiophen molecule. In relation to the benzene ring, the thiodiimide group in the ground state of the molecule may behave as a weak π donor.[110]

According to the same calculation,[110] the order of the SN π-bond in diphenylthiodiimide is 0.659. The study of the π-bond orders in dimethylthiodiimide and heterocycles containing the N=S=N groups such as naphtho[1,8,*cd*]-1,2,6-thiadiazine, benzo-2,1,3-thiadiazole and 2,1,3-thiadiazole in terms of the CNDO/2 approximation, with and without the inclusion of the 3*d* AO of sulphur in the basis set, has shown that, although there is a definite amount of the SN double bond character in 2,1,3-thiadiazole (the SN π-bond order is 0.428 or 0.379; here and henceforth the first value has been obtained taking into account 3*d* AO of sulphur), its structure is best described by a formula with bivalent sulphur. On passing to benzo-2,1,3-thiadiazole, the amount of the SN double bond character increases, but the SN π-bond order (0.542 and 0.481) is nevertheless lower than in naphtho-[1,8-*cd*]-1,2,6-thiadiazines (0.641 and 0.647) in which it almost agrees with the π-bond order in dimethylthiodiimide (0.651 when account is taken of the 3*d* AO of sulphur). The latter factor can be interpreted as evidence in support of the thiodiimide structure, with quadrivalent sulphur, of naphtho-[1,8-*cd*]-1,2,6-thiodiazine. When the 3*d* AO of sulphur are included in the basis set, the SN π-bond order does not change in this compound, from which it follows that the quadrivalent state of sulphur does not by itself indicate, as is usually assumed, the involvement of the 3*d* AO of sulphur in bonding.[113] Indeed the π-bond in organic thiodiimides, as well as in other heterocumulenes containing quadrivalent sulphur, is described with the aid of MO of the allyl type,[1] made up in the case of thiodiimides of the *p* AO of the nitrogen and sulphur atoms oriented at right angles to the plane of the molecule.

(b) Vibrational spectroscopic data. Special studies[77,114,115] of thiodiimides enriched with ^{15}N have shown that the stretching vibration frequencies of the SN bonds are extremely sensitive to the character of the substituents to which the thiodiimide group is linked (Table 4), but it is difficult to establish general characteristic features. Thus, on passing from dialkyl- to diaryl-thiodiimides, the symmetrical SN stretching vibration frequency falls, while the antisymmetrical frequency increases.[114] The frequency ν_{as}(SN) for dibenzoylthiodiimide is in the range of values for diarylthiodiimides, while ν_s(SN) for the benzoyl derivative is much greater than for aryl derivatives (Table 4). On passing from diaryl- to bis(polyfluoroaryl)-thiodiimides, the stretching vibration frequencies of the SN bond increase, which probably indicates an increase of the SN bond force constants and orders as a consequence of the weakening of the p_π–p_π interaction between NSN and the polyfluoroaryl group compared with the aryl group.[115]

Table 4. Vibration frequencies (cm^{-1}) of the thiodiimide group in the compounds R–N=S=N–R.

R	ν_{as}(SN)		ν_s(SN)		δ(NSN)		Refs.
	IR	Raman	IR	Raman	IR	Raman	
Alk	1192–1218	1189–1216	1055–1096	1056–1082	—	—	[114]
Me_3Si	1261	1261	1140	1140	435	436	[88]
Ar	1252–1300	1250–1293	958–980	960–984	778–804	792–804	[114]
Ar_f	1445*	1430–1450	**	1160–1205	845–855	854–862	[115]
PhCO	1275	—	1170	—	—	—	[77]

*The position of the band is difficult to determine owing to its overlap with the bands due to the polyfluoroaryl group.[115]
**Absent from the infrared spectrum.[115]

On excitation of the Raman spectrum of di-*p*-tolylthiodiimide by radiation at a wavelength of 458 nm (the maximum of the long-wavelength absorption in the electronic spectrum of this compound is at 434 nm[51]), a resonance increase in the intensities of all the bands occurs in the range 700–1400 cm^{-1},

which indicates an effective delocalisation of the π-bonding in the molecule. The intensities of the ν_s(SN) and ν_s(PhN) bands increase to the greatest extent, which indicates that the long-wavelength absorption band in the electronic spectrum of di-*p*-tolylthiodiimide is associated with a transition accompanied by an appreciable redistribution of charge between the N=S=N group and the aromatic rings.[114] This observation agrees well with the results of a theoretical interpretation of the electronic spectra of diarylthiodiimide[110] (see previous Section).

The substituents X in the compounds 4-$O_2NC_6H_4N$=S=NC_6H_4X-4 decrease the symmetrical stretching vibration frequency of the nitro-group in their infrared spectra, while electron-accepting substituents behave in different ways—they either decrease or increase the frequency, $\Delta\nu$ being in no way correlated with the Taft constant. This led to the conclusion[109] that there is no direct transmission of the effect of the conjugation of the substituent X to the second ring via the thiodiimide group and that an interaction of this kind is limited to the sulphur atom.

From the relation between the antisymmetrical stretching vibration frequency of the nitro-group and the constant σ_p^0, the σ_p^0 for the 4-$O_2NC_6H_4N$=S=N and C_6H_5CON=S=N groups were calculated from the IR spectroscopic data for bis(4-nitrophenyl)- and *N*-benzoyl-*N'*-4-nitrophenyl-thiodiimides as 0.2 and -0.3 respectively, from which it follows that the first group is electron-accepting and the second is electron-donating in relation to the benzene ring.[78]

The inductive influence of the C_6H_5N=S=N group has been estimated from the IR spectrum of *N*-benzenesulphonyl-*N'*-phenylthiodiimide on the basis of the finding that the average stretching vibration frequency of the SO_2 group is sensitive mainly to *I* effects.[78] It was assumed that $\nu_s(SO_2)$ and $\nu_{as}(SO_2)$ are 1164 and 1248 cm^{-1} respectively. The frequency $\nu_s(SO_2)$ = 1164 cm^{-1} agrees with the results of other studies dealing with the IR spectra of *N*-arenesulphonyl-*N'*-aryl- or bis(arenesulphonyl)-thiodiimides,[65,109] but the frequency $\nu_{as}(SO_2)$ = 1248 cm^{-1} disagrees with these results. According to Wucherpfennig and Kresze,[65] $\nu_{as}(SO_2)$ in the IR spectra of thiodiimides of the type $(R-SO_2-N=)_2S$ is in the range 1340–1355 cm^{-1}, while according to Lutskii et al.[109] the band at 1330 cm^{-1} in the spectrum of *N*-benzenesulphonyl-*N'*-phenylthiodiimide is associated with $\nu_{as}(SO_2)$. The conclusion[78] that $\sigma_I \cong 0.2$ for the C_6H_5N=S=N group becomes controversial as a result of this finding.

The vibrational spectra of compounds with sulphur–nitrogen chains longer than N=S=N have not been studied systematically. If the known group frequencies of the F_3CS fragment are excluded from the IR spectrum of bis(trifluoromethanesulphonyl)thiodiimide, we find that ν_{as}(NSN) = 940 cm^{-1}, ν_s(NSN) = 651 cm^{-1}, and δ(NSN) = 503 cm^{-1}.[116] The explanation of such a marked decrease of the frequencies is based on the concept of the pulsation of the entire SNSNS fragment, in which mainly nitrogen vibrates as a consequence of the large difference between the masses and the π-electron system of the central (multiple) SN bonds extend over the entire sulphur–nitrogen skeleton, which equalises the bond orders to 1.5. The appreciable decrease of the ν_{as}(SN) frequency on passing from ArSN=S=N–$SiMe_3$ (ν_{as} = 1194–1202 cm^{-1}) to $(ArSN=)_2S$ (ν_{as} = 1138–1146 cm^{-1}) and $(ArSN=S=N)_2S$ (ν_{as} = 1080–1100 cm^{-1}) has been explained analogously.[2] An alternative explanation is associated with the possible difference between the molecular geometries: if bis(arenesulphonyl)thiodiimides have the *cis,cis*-geometry, then *N*-arenesulphenyl-*N'*-trimethylsilylthiodiimides are most likely to have the *cis,trans*-geometry.[2]

The concept of the decrease of the SN vibration frequency is a consequence of the increased electron delocalisation in the sulphur–nitrogen chain with increase of its length appears attractive but apparently agrees poorly with structural data. On passing from diaryl- to bis(arenesulphenyl)-thiodiimides, the lengths of the bonds in the central N=S=N units hardly change and the complete equalisation of the π-bonds suggested by Haas and Schott[116] does not exist (see above).

(c) ^{15}N NMR spectroscopic data. In this Section all the chemical shifts quoted in the original studies relative to different standards have been recalculated in relation to nitromethane; the positive values correspond to upfield shifts.

The ^{14}N NMR signal of diphenylthiodiimide (solution in ether) is at ~72 p.p.m.,[117] whereas the ^{15}N NMR signal is at ~114 p.p.m. [solution in dimethyl sulphoxide (DMSO)] according to other data.[102] It is known that, within the limits of experimental error, the chemical shifts are the same for the ^{14}N and ^{15}N nuclei when the spectra are recorded under identical conditions.[118] The discrepancy between the results of Yavari et al.[102] and Mason et al.[117] is too great to be caused by the difference between the solvents, the chemical shift quoted for nitrogen in diphenylthiodiimide in these investigations is clearly erroneous. Since it is known[119–121] that certain thiodiimides interact with DMSO, the result of Mason et al.[117] appears to be less reliable.

Comparison with the closest analogues, namely *N*-sulphinylarylamines, has shown that the NMR signals of nitrogen in the spectra of diarylthiodiimides are located in a somewhat higher field. For example, the ^{14}N NMR signal of diphenylthiodiimide has undergone an upfield shift relative to the signal of *N*-sulphinylaniline by approximately 18 p.p.m.[117,122] It is of interest to note that the chemical shift of the ^{14}N NMR signal in the spectrum of diphenylthiodiimide is the same as that of pyrimidine.[117]

On passing from diphenylthiodiimide to *N*-pentafluorophenyl-*N'*-phenylthiodiimide and further to bis(pentafluorophenyl)thiodiimide, the ^{15}N NMR signal undergoes an upfield shift.[50] Analogous shifts on passing from hydrocarbon analogues to perfluorinated derivatives are observed also for many other classes of aromatic nitrogen-containing compounds.[50,123,124] Comparison of ^{15}N NMR and S K_β spectroscopic data for thiodiimides has shown that the chemical shift of the nitrogen signal is influenced primarily by the changes in the character of the interaction of the nitrogen atom with aromatic rings and not with sulphur atoms.[50] According to a calculation in terms of the CNDO/2 approximation[110] and ^{13}C NMR data,[125] the thiodiimide group is electron-donating in relation to the benzene ring ($\sigma^+ = -0.1$ for the C_6H_5N=S=N group[125]). The weakening of the p_π–p_π interaction of the NSN group and the aromatic rings on passing from diaryl- to bis(polyfluoroaryl)-thiodiimides[50,115] therefore entails an increase of π-electron density at the nitrogen atom. An increase of electron density (negative charge) on the nitrogen atom leads to a decrease of the absolute value of the paramagnetic term in the expression for the shielding constant and hence to an increase of the shielding and an upfield shift of the ^{15}N NMR signal.[118]

Table 5. The constants σ_R^0 and σ_I of complex substituents R containing the thiodiimide group.*

R	σ_R^0	σ_I	R	σ_R^0	σ_I
C_6F_5NSN	−0.03	−0.16	C_6H_5NSNS	0.01	0.17
C_6H_5NSN	−0.11	−0.14	C_6F_5SNSNS	0.02	0.22
C_6F_5SNSN	−0.21	−0.10	C_6H_5SNSNS	−0.03	0.13
C_6H_5SNSN	−0.16	−0.04	t-BuNSN	−0.48	0.73
C_6F_5NSNS	0.10	−0.08			

*According to the data of Brands and Golloch.[127]

Apart from the effective atomic charge, the chemical shifts of nitrogen depend on the average energy ΔE of the electronic excitations which correspond to the circulation of the electron around the nucleus when the electron is described by a point charge. In this case the lower ΔE, the greater the deshielding. The energy ΔE can be estimated from the energy of the long-wavelength bands in the electronic absorption spectra associated with the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions.[123] The additional stabilisation of the σ MO of planar molecules or groups relative to π MO when the hydrogen atoms are fully substituted by fluorine (the "perfluoro-effect") leads to a hypsochromic band shift in the electronic absorption spectra caused by the $\sigma \rightarrow \pi^*$ and $n \rightarrow \pi^*$ excitations.[123,126] On passing from diphenyl- to bis(pentafluorophenyl)-thiodiimide, the long-wavelength absorption band in the electronic spectrum shifts towards shorter wavelengths (Table 3). This band is usually attributed to $\pi \rightarrow \pi^*$ excitations[110,111] but in the spectra of diaryl- and bis(polyfluoroaryl)-thiodiimides it is fairly broad and apparently can mask the band associated with the $n \rightarrow \pi^*$ excitations. If this is indeed so, on passing from diphenyl- to bis(pentafluorophenyl)thiodiimide, ΔE increases, which also leads to an upfield shift of the ^{15}N NMR signal.

(d) Data obtained by other methods. The constants σ_R^0 and σ_I presented in Table 5 have been calculated from the ^{19}F NMR spectroscopic data for thiodiimides containing the pentafluorophenyl substituent.[127]

Compounds of the type $C_6H_5SO_2N{=}S{=}NC_6H_4X\text{-}4$, $4\text{-}O_2NC_6H_4N{=}S{=}NC_6H_4X\text{-}4$, $(ArN{=})_2S$, and $C_6H_5CON{=}S{=}NAr$ have been investigated by the method of dipole moments.[18,109] The results were interpreted on the assumption that the molecules exist either in the *cis,cis*-configuration[109] or *trans,trans*-configurations.[78] However, thiodiimides with aromatic substituents exist in solution in the form of an equilibrium mixture of the *cis,trans*- and *trans,trans*-isomers with the *cis,trans*-isomer predominating.[48] This finding casts doubt on the conclusions[78,109] based on the study of the dipole moments.

In the mass spectrum of the *N*-pentafluorophenyl-*N'*-phenylthiodiimides the peaks of the $C_6F_5N^+$ and $C_6H_5NS^+$ ions predominate over the peak of the $C_6F_5NS^+$ ion. Such fragmentation is explained by the powerful polarising action of the pentafluorophenyl group, which weakens one of the sulphur–nitrogen bonds in accordance with the scheme[128]

$$Ph_f{-}N{=}S{=}N{-}Ph \longleftrightarrow Ph_f{-}\bar{N}{-}\overset{+}{S}{=}N{-}Ph \dashrightarrow \xrightarrow[-2e^-]{+e^-} Ph_f{-}\dot{N}{-}\overset{+}{S}{=}N{-}Ph\,.$$

IV. CHEMICAL PROPERTIES

The most characteristic reactions of organic compounds containing the thiodiimide group are those with nucleophiles and cycloaddition. The reactivity of the N=S=N fragment depends significantly on the character of the groups linked to it and as a rule decreases with increasing electronegativity of the latter. According to frontier orbital theory, in the reactions of nucleophiles with electrophiles (in the given case with thiodiimides) the interaction of the HOMO of the nucleophile with the LUMO of the electrophile is most important.[129] However, the excited states of the molecules of organic thiodiimide have been scarcely investigated. Different conclusions about the true mechanisms of many reactions with their participation are therefore at present hardly possible. In particular, one cannot rule out the possibility that not all reactions with what are formally nucleophiles do indeed involve nucleophilic attack on the sulphur atom of the thiodiimide group. It is extremely likely that many reactions of thiodiimides proceed with the intermediate participation of thionitroso-compounds.

It has been shown for a large number of examples[130] that the chemical properties of organic thiodiimides are close to those of sulphur dioxide and *N*-sulphinylamines. At first sight, this is entirely natural, since both thiodiimides and *N*-sulphinylamines are aza-analogues of SO_2. On the other hand, it has been shown that the positive charges on the sulphur atoms and the distribution of the 3*p* electrons of sulphur among the MO are appreciably different for SO_2, *N*-sulphinylarylamines, and thiodiimides with aromatic substituents at the nitrogen atom.[131] Hence, one may imagine that the properties of the excited states can also differ and one should therefore expect some differences in reactivity. The latter do indeed exist. For example, whereas tris(trimethylstannyl)amine forms an adduct with bis(pentafluorophenyl)-thiodiimide,[132] in its reaction with *N*-sulphinylpentafluoroaniline it forms *NN*-bis(trimethylstannyl)pentafluoroaniline and trimethylstannylthionylimide.[83]

1. Thermolysis

Dimethylthiodiimide decomposes slowly even at room temperature.[16,17] The t-alkyl derivatives are more stable. The pyrolysis of di-t-butylthiodiimide at 265 °C results in a 60% yield of isobutene. The reaction is apparently concerted. The pyrolysis of diphenylthiodiimide at 200 °C affords azabenzene with a 66% yield.[133] It has been suggested that this reaction takes place with participation of a thiadiazirine intermediate.[113] The thermolysis of bis(2,4-di-t-butyl-6-methylphenyl)thiodiimide in boiling benzene leads to the corresponding arylamine and benzothiazole.[59]

2. Interaction with Nucleophiles

All organic thiodiimides tend to hydrolyse; the hydrolysis products are the corresponding amines or amides and sulphur dioxide. Bis(arylsulphenyl)thiodiimides, whose hydrolysis leads to arenethiols, sulphur dioxide, and ammonia are an exception.[134] The hydrolytic stability of thiodiimides decreases with enhancement of the electron accepting properties of the substituents at the N=S=N groups. Thus bis(arenesulphinyl)- and bis(alkoxycarbonyl)-thiodiimides are readily hydrolysed even by atmospheric moisture,[64,79] while bis(pentafluorophenyl) thiodiimide hydrolyses faster by more than an order of magnitude than bis(4-chlorophenyl)-thiodiimide under identical conditions.[49]

The interaction of bis(benzenesulphonyl)thiodiimide with aliphatic alcohols yields esters of *NN'*-bis(benzenesulphonyl)-amidoiminosulphurous acid.[135] Ditosylthiodiimide interacts analogously with benzyl alcohol and oximes. In this case the esters formed are unstable and decompose giving rise to the final reaction products:[136]

$$(TosN{=})_2S \xrightarrow{PhCH_2OH} TosN{=}S(HNTos)OCH_2Ph \rightarrow \rightarrow TosNSO + PhCH_2NHTos;$$

$$(TosN{=})_2S \xrightarrow{PhCH{=}NOH} TosN{=}S(HNTos)ON{=}CHPh \rightarrow \rightarrow TosNSO + TosNH_2 + PhCN;$$

$$(TosN{=})_2S \xrightarrow{Ph_2C{=}NOH} TosN{=}S(HNTos)ON{=}CPh_2 \rightarrow \rightarrow TosNSO + PhC(=NPh)HNTos.$$

Ditosylthiodiimide interacts with aliphatic sulphides, including cyclic sulphides, as nucleophiles. The products are the corresponding *SS*-dialkyl-*N*-tosylsulphimines and elemental sulphur.[137]

Bis(arenesulphonyl)thiodiimides react with compounds containing the O=X bond (X = C, S, P, or As):[120]

$$(ArSO_2{-}N{=})_2S \xrightarrow{-SO_2}$$

$\xrightarrow{Ar'CHO}$ $Ar'CH{=}N{-}SO_2Ar$;

$\xrightarrow{PhCONMe_2}$ $PhC(=N{-}SO_2Ar)NMe_2$;

$\xrightarrow{HCONMe_2}$ $Me_2NCH{=}N{-}SO_2Ar$;

$\xrightarrow{Me_2SO}$ $Me_2S{=}N{-}SO_2Ar$;

$\xrightarrow{R_3PO}$ $R_3P{=}N{-}SO_2Ar$;

$\xrightarrow{Ph_3AsO}$ $Ph_3As{=}N{-}SO_2Ar$;

R=Me, Et, Ph.

Dibenzoylthiodiimide reacts analogously with DMSO.[121] The interaction apparently begins with nucleophilic attack by the O atom of the O=X group on the S atom of the thiodiimide group:

$$(ArSO_2N{=})_2S \xrightarrow{R_nX{=}O} \left[\begin{array}{c} ArSO_2\bar{N}{-}S{=}NSO_2Ar \\ | \\ R_n\overset{+}{X}{-}O \end{array}\right] \rightarrow$$

$$\rightarrow \left[\begin{array}{c} ArSO_2N{-}S{=}NSO_2Ar \\ | \quad | \\ R_nX{-}O \end{array}\right] \xrightarrow{-R_nX{=}NSO_2Ar}$$

$$\rightarrow [ArSO_2{-}NSO] \xrightarrow[-SO_2]{R_nX{=}O} R_nX{=}NSO_2Ar .$$

In those cases where the intermediate *N*-sulphinylamine does not react with the oxygen-containing compound, the reaction stops in the first stage. For example, the interaction of *N*-benzenesulphenyl-*N'*-phenylthiodiimide with DMSO results in the formation of *N*-benzenesulphenyl-*SS*-dimethylsulphimine and *N*-sulphinylaniline.[120] The reaction of ditosylthiodiimide with sulphoxides leads to similar products, namely *SS*-disubstituted *N*-tosylsulphimines and *N*-sulphinyltoluene-*p*-sulphonamide. The conversion of chiral sulphoxides into sulphimines in different solvents proceeds via different mechanisms. In pyridine at 0 °C the reactions are termolecular and proceed with inversion of the configuration at the sulphur atom; in benzene the reactions take place with retention of the configuration and are bimolecular.[119]

The reactivity of thiodiimides with respect to compounds having an O=X bond decreases with decreasing electronegativity of the substituents at the nitrogen atom. Thus diarylthiodiimides containing nitro-groups or chlorine atoms in the 4,4'-positions in the rings react with aldehydes like the bis(arenesulphonyl)derivatives, while diphenylthiodiimide and diarylthiodiimides containing electron-donating substituents do not react with aldehydes, sulphoxides, and phosphine oxides.[120]

Dibenzoylthiodiimide does not react with aromatic aldehydes, but in the presence of benzamide the reaction proceeds readily with formation of *NN'*-diaroylamidals. The thiodiimide behaves simultaneously as a dehydrating agent and an additional source of the amide:[121]

$$ArCHO + PhCONH_2 + (PhCON{=})_2S \xrightarrow{-SO_2} ArCH(NHCOPh)_2$$

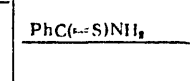
Dibenzoylthiodiimide reacts with trichloroacetaldehyde to form *NN'*-diacetylchloral amidal. In the presence of aluminium chloride, the reaction leads to *N*-benzoylchloral imine.[121]

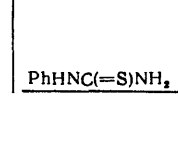
Phosphine sulphides and dialkylthioamides of carboxylic acids react with bis(arenesulphonyl)thiodiimides like the corresponding oxygen-containing compounds to form phosphazo-compounds or amidines. On reaction with bis(arenesulphonyl)thiodiimides, thiobenzamide and phenylthiourea are converted into 1,2,4-thiadiazole and 1,2,4-thiadiazolidine derivatives:[120]

$$(ArSO_2N{=})_2S{-}$$

$\xrightarrow{R_3P{=}S}$ $R_3P{=}NSO_2Ar$;

$\xrightarrow{RC(=S)NR_2}$ $RC(=NSO_2Ar)NR_2$;

$\xrightarrow{PhC(=S)NH_2}$  ;

$\xrightarrow{PhHNC(=S)NH_2}$  .

NN-Dibenzoylarenesulphonamides and arenesulphonylphthalimides have been obtained respectively on heating bis(arenesulphonyl)thiodiimides with benzoic or phthalic anhydride.[120]

The reaction of bis(benzenesulphonyl)thiodiimide with dialkylamines results in the formation of dialkylammonium salts. The *NN*-dialkylamides of *N'N''*-bis(benzenesulphonyl)-amidoiminosulphurous acid are probably formed in the first stage. They have acid properties and react with a second dialkylamine molecule.[135] *N*-Aryl-*N'*-benzenesulphonylthiodiimides are symmetrised in the presence of secondary amines; the symmetrisation is accompanied by the formation of the dialkylammonium salts from the bis(benzenesulphonyl) derivative:[135]

$$PhSO_2{-}N{=}S{=}N{-}Ar \xrightarrow{Alk_2NH} (ArN{=})_2S +$$

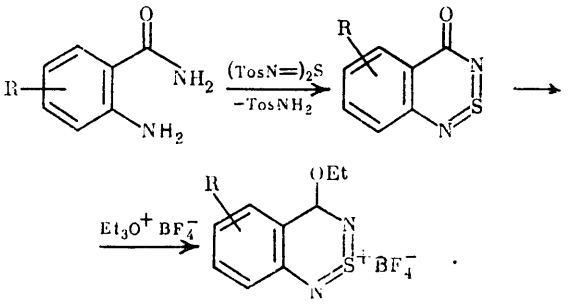
$$[(PhSO_2N)_2SNAlk_2]^- [Alk_2NH_2]^+ .$$

Tris(trimethylstannyl)amine and some of its derivatives add to bis(polyfluoroaryl)- and bis(arenesulphonyl)-thiodiimides in equimolar proportions:[132]

$$(R{-}N{=})_2S \xrightarrow{(Me_3Sn)_2NR'} \begin{array}{l} Me_3SnN \diagup R \\ \qquad\quad \diagdown S{=}NR' \\ Me_3SnN \diagdown R \end{array} ;$$

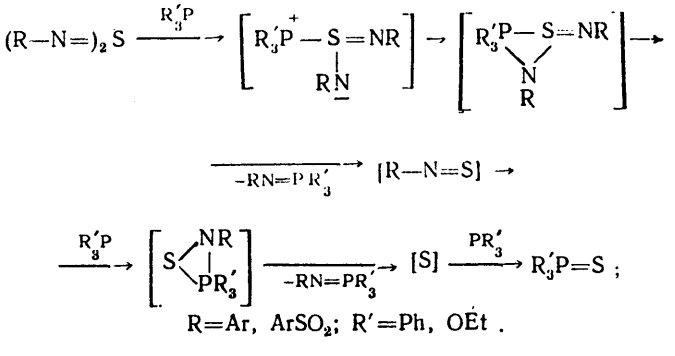
$R=C_6F_5$, $R'=Me_3Sn$, Me, C_6F_5; $R=4\text{-}ClC_6H_4SO_2$, $R'=Me$.

The interaction of thiodiimides with aromatic amines was examined above (see Section II). The reaction of bis(benzenesulphonyl)thiodiimide with *o*-phenylenediamine leads to benzo-2,1,3-thiadiazole.[61] Substituted 2-amino-benzamides interact with ditosylthiodiimide to form cyclic products whose alkylation gives rise to benzo-2,1,3-thiadiazinium salts:[138]

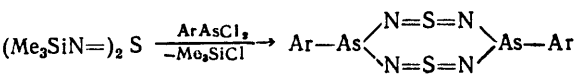


Bis(arenesulphonyl)- and diaryl-thiodiimides react with phosphines and phosphites. The interaction of bis(arenesulphonyl)thiodiimides and diarylthiodiimides containing electron-accepting substituents in the ring with triphenylphosphine leads to triphenylphosphine sulphide and phosphazo-compounds.[120] On heating with triphenylphosphine, *N*-t-butyl-*N'*-trimethylsilylthiodiimide decomposes analogously to the corresponding iminophosphoranes and phosphine sulphide.[33] The reactivity of thiodiimides towards phosphines diminishes with increasing electronegativity of the substituents at the nitrogen atoms. Thus triphenylphosphine reacts exothermically with bis(arenesulphonyl)thiodiimides, while the reaction with bis(4-nitrophenyl)thiodiimide takes place only on heating. Diarylthiodiimides containing electron-donating substituents do not react with triphenylphosphine.[120]

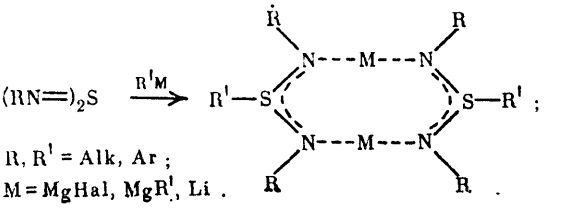
The interaction of bis(arenesulphonyl)- and diaryl-thiodiimides with phosphites is accompanied by the formation of phosphorothioates and phosphazo-compounds.[43,120] The initial stage of the reaction of bis(arenesulphonyl)- and diarylthiodiimides with phosphines and phosphites apparently consists in the nucleophilic attack by the phosphorus atom on the sulphur:[43,120]



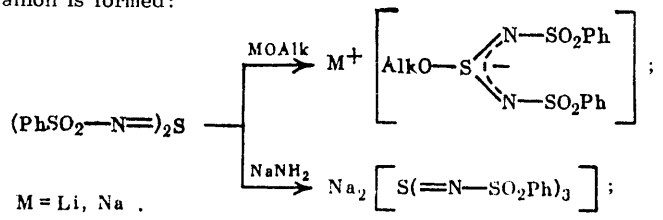
The reaction of triphenylphosphine with dibenzoylthiodiimide takes place differently and leads to benzonitrile, elemental sulphur, and triphenyl-phosphine oxide.[121] The interaction of bis(trimethylsilyl)thiodiimide with phenyl- and mesityl-dichloroarsines leads to the corresponding dithiatetrazadiarsocines:[139]



Organomagnesium and organolithium compounds add quantitatively to dialkyl- and diaryl-thiodiimides. This reaction has been used as the basis of a convenient method for the quantitative analysis of organometallic compounds:[140]

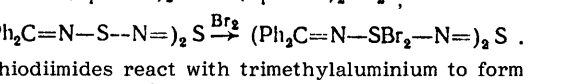


Bis(arenesulphonyl)- and bis(trifluoromethanesulphonyl)-thiodiimides react with lithium and sodium alkoxides to form stable salts of anions and contain a tricoordinate sulphur atom according to X-ray diffraction data. The interaction with dry CsF proceeds analogously. When bis(benzenesulphonyl)thiodiimide is treated with sodium amide, a stable salt containing the tris(benzenesulphonylimido)sulphide anion is formed:[141]



3. Interaction with Electrophiles

When thiodiimides are allowed to react with fluorine, the *SS*-difluoro-derivatives are obtained.[142] Bromination of 1,5-bis(diphenylmethyleneamino)trithiodinitride takes place apparently in the 1,5-positions in the sulphur–nitrogen fragment:[69]

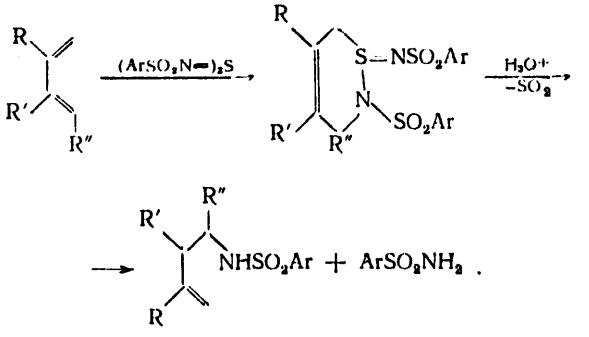


Diarylthiodiimides react with trimethylaluminium to form complexes of the type $\{Me_2Al[ArNS(Me)NAr]\}_2$, in which the sulphur atom is methylated.[143]

4. Cycloaddition Reactions

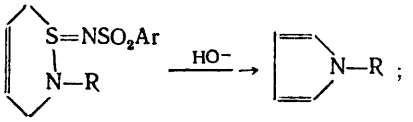
Organic thiodiimides are capable of undergoing the $[4\pi + 2\pi]$ and $[2\pi + 2\pi]$-cycloaddition reactions. The former are represented by the 1,4-cycloaddition to 1,3-dienes and the 1,3-cycloaddition to diphenylketen and the latter by the 1,2-cycloaddition to heterocumulenes and olefins.

Bis(arenesulphonyl)thiodiimides react exothermically with 1,3-dienes at room temperature to form 1-arenesulphonyl-imino-2-arenesulphonyl-3,6-dihydro-1,2-thiazines.[64,65,144] Acid hydrolysis of the adduct affords arenesulphonamides, sulphur dioxide, and arenesulphonyliminobut-3-enes:[144]



Bis(alkoxycarbonyl)- and diaroyl-thiodiimides react analogously with dienes.[77,79]

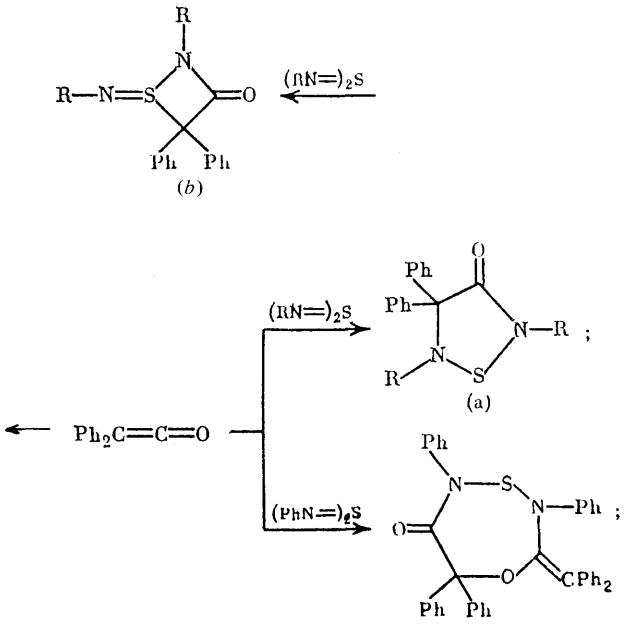
Asymmetric thiodiimides having non-equivalent SN bonds, for example *N*-alkyl- and *N*-aryl(heteryl)-*N'*-arenesulphonylthiodiimides react only via the SN bond remote from the sulphonyl group.[63,80,145] Acid hydrolysis of thiazines proceeds in the same way as for 2-arenesulphonyl- and 2-alkoxycarbonyl-derivatives, but treatment of 1-arenesulphonylimino-2-aryl(heteryl)-3,6-dihydro-1,2-thiazines with an alcoholic solution of alkali makes it possible to obtain *N*-arylpyrroles[145] and 2-(1-pyrrolyl)pyridines:[63]



R=Ar, 2-Py .

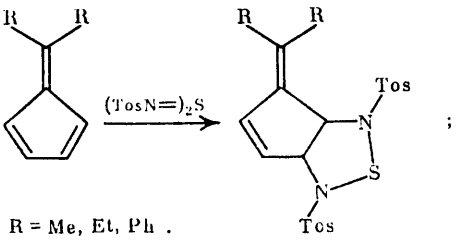
The rate of reaction of thiodiimides with 1,3-dienes depends on the character of the substituent at the nitrogen atom. Whereas bis(arenesulphonyl)thiodiimides react with evolution of heat, *N*-aryl-*N'*-arenesulphonylthiodiimides react only on heating. Electron-accepting substituents in the aryl group accelerate the reaction, while electron-donating substituents retard it.[145] Dialkyl-, diaryl-, and *N*-alkyl-*N'*-bromo-, and *N*-benzenesulphenyl-*N'*-benzenesulphonyl-thiodiimides do not enter into the cycloaddition reaction with 1,3-dienes.[18,68,80]

Ditosyl-, diphenyl, and bis(4-ethoxycarbonylphenyl)-thiodiimides react with diphenylketen at 70–80 °C to form 1,3-adducts with reduction of sulphur(IV) to sulphur(II)—2,5-diaryl[bis(arenesulphonyl)]-3,3-diphenyl-1,2,5-thiadiazolidin-4-ones are formed.[146–148] At −15–0 °C the reaction of diphenylketen with ditosylthiodiimide and di-t-butylthiodiimide proceeds as 1,2-cycloaddition,[146,148] while the reaction with diphenylthiodiimide at 6–8 °C results in the formation of perhydro-2-diphenylmethylene-3,5,7,7-tetraphenyl-1,4,3,5-oxathiadiazepin-6-one, whose structure has been confirmed by X-ray diffraction:[148]



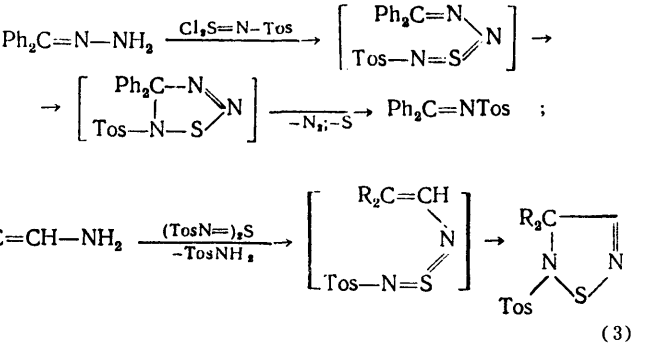
(a) R = Tos, Ph, 4-EtOCOC$_6$H$_4$;
(b) R = Tos, t-Bu.

Di-t-butylthiodiimide reacts with dichloroketen at 70 °C to form a 1,2-cycloaddition product.[149] Dialkyl- and diarylthiodiimides react with bis(trifluoromethyl)thioketen to form the corresponding keten imines. No data confirming the mechanism have been obtained, but one cannot rule out the possibility that the reaction proceeds via five- or four-membered rings—the products of the initial cycloaddition of the thiodiimides.[150] Ditosylthiodiimide enters into a 1,3-cycloaddition reaction with 6,6-disubstituted fulvenes at −10–−15 °C:[151]



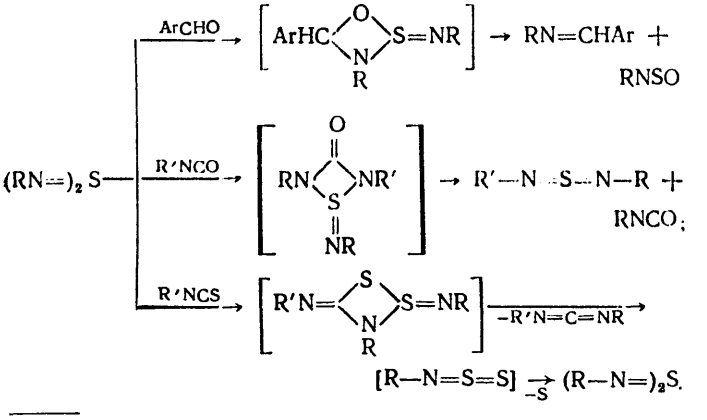
R = Me, Et, Ph .

An unusual intramolecular 1,3-cycloaddition of the thiodiimide group to the azomethine bond probably takes place in the reaction of *SS*-dichloro-*N*-tosylsulphimine with benzophenone hydrazone, which leads to a Schiff base, elemental nitrogen, and sulphur.[152] The reaction [153]



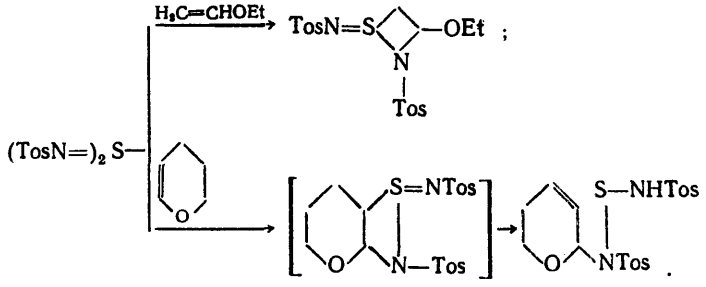
(3)

probably includes the transamination and intramolecular cycloaddition stages. Certain reactions of di-t-butylthiodiimide, such as those with aldehydes,§ isocyanates, and isothiocyanates probably proceed via the [2π + 2π]-cyclo-addition stage. The cyclic adducts decompose in such a way that fragment exchange reactions are observed ultimately:[154]

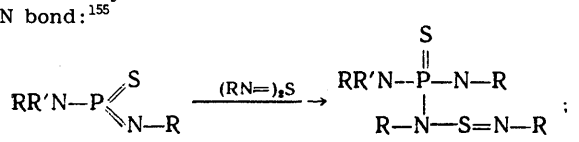


§ Levchenko and Ugarov[120] regard this reaction as nucleophilic (see Subsection 2).

Yet another example of 1,2-cycloaddition is provided by the reaction of ditosylthiodiimide with "electron-rich" olefins (vinyl ethers):[1,137]

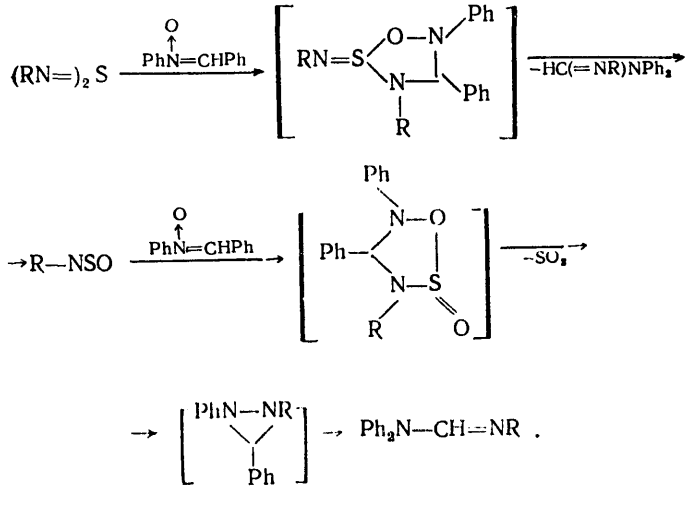


It is of interest to note that thiodiimides undergo 1,2-cycloadditon not only to a carbon–carbon double bond but also to a P=N bond:[155]

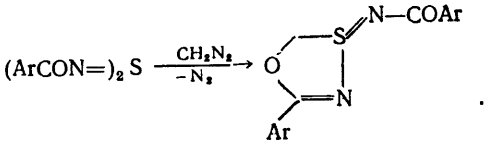


R = t-Bu, R′ = Me_3Si .

Bis(arenesulphonyl)- and dibenzoyl-thiodiimides readily react with *CN*-diphenylnitrone to form respectively *N*-arenesulphonyl-*N′N′*-diphenylformamidines[120] and *N*-benzoyl-*N′N′*-diphenylformamidines.[121] One cannot rule out the possibility that the reaction begins with 1,3-dipolar cycloaddition of the nitrone at the thiodiimide group and involves subsequent decomposition of the adduct:



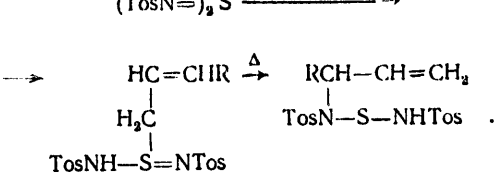
The reaction of diaroylthiodiimides with diazomethane, leading to 3-aroylimino-5-aryl-1,3,4-oxathiazolines,[156] probably includes cheletropic cycloaddition of singlet carbene to the quasi-buta-1,3-diene system formed by the C=O and S=N bonds of the initial thiodiimide:



Theoretical study of the cycloaddition reactions of thiodiimides has shown that the thermal 1,4- and 1,3-cycloaddition reactions are symmetry-allowed; the 1,2-cycloaddition is symmetry-allowed only for the *cis,trans*-isomer and can take place via the overlap of the HOMO of the thiodiimide and the LUMO of the olefin.[113]

5. The Ene Synthesis

Ditosylthiodiimide reacts with many alkenes to form allylsulphinamides capable of undergoing a 2,3-sigmatropic rearrangement on further heating:[119,157,158]

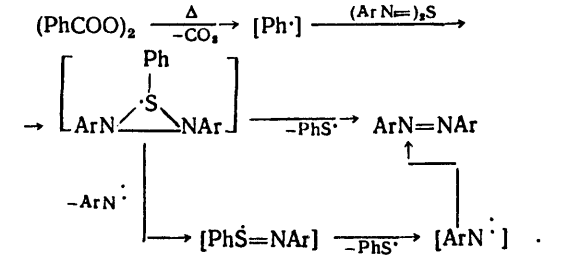


The relative reactivities of ene compounds and the regio- and stereo-selectivity of the reaction have been studied in detail.[158] The preparative application of this reaction for the synthesis of primary allylamines has been examined in a review.[159]

6. Interaction with Free Radicals

Di-t-butylthiodiimide readily combines with radicals of the type $R_n\dot{M}$ [for example, $F_3\dot{C}$, $Me_3\dot{S}i$, $(n\text{-}Bu)_3\dot{S}$, $F_3C\dot{S}$, and $(EtO)_2\dot{P}O$] with formation of the relatively stable nitrogen-centred radical t-Bu$\dot{N}$SN(Bu-t)MR_n.[160]

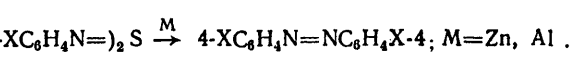
The interaction of diarylthiodiimides with the phenyl radical proceeds differently when equimolar amounts of benzoyl peroxide and the thiodiimide are refluxed in benzene. The reaction leads to biphenyl, diphenyl disulphide, and the corresponding azo-compound. The mechanism proposed for it is illustrated in Scheme (4). Arylnitrenes also participate in the reaction to a slight extent:[161]



(4)

7. Elimination of Sulphur by Metals

The reaction of diphenylthiodiimide with metals leads to azobenzene, probably via an intramolecular pathway, since a mixture of analogues (with X=X and X=Ph in the Scheme presented below) gives rise to azobenzene and 4,4′-diphenylazobenzene; 4-phenylazobenzene is not then formed:[41]



8. Oxidation

When *N*-2-nitrobenzenesulphenyl-*N'*-tosylthiodiimide was oxidised with lead tetraacetate, potassium permanganate, or selenium dioxide, toluene-*p*-sulphonamide and bis(2-nitrophenyl) disulphide were identified.[68] The interaction of dimethyl- and di-t-butyl-thiodiimides with ozone yielded the corresponding nitroalkanes and *N*-sulphenylalkylamines:[25]

$$(AlkN=)_2S \xrightarrow{[O_3]} AlkNO_2 + AlkNSO\ .$$

9. Reduction

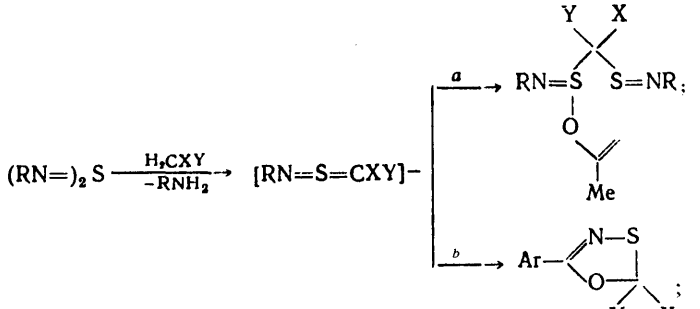
NN'-Bis(arenesulphonyl)-, *NN'*-diaroyl-, and *N*-aryl-*N'*-benzene-sulphonyl-thiodiimides are readily reduced by thiophenols:[136,162]

$$R{-}N{=}S{=}N{-}R' \xrightarrow[-(ArS)_2]{ArSH} R{-}NH{-}S{-}NH{-}R'\ .$$

Ditosylthiodiimide is also reduced to bis(*N*-tosylamino)sulphane by hyrazobenzenes, hydroquinone, catechol, and dihydronaphthalenes—in most cases under mild conditions.[136]

10. Interaction with CH-acids

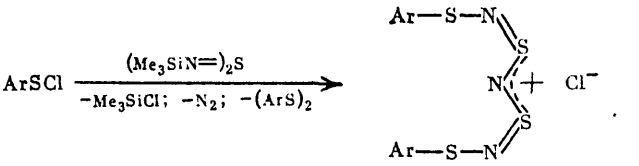
NN'-Bis(arenesulphonyl)thiodiimides react with acetylacetone in acetoacetic and malonic esters in proportions of 1:1 to form 4,6-bis(arenesulphonylimino)-3-oxa-4,6-diathiacyclohex-1-enes.[163] When dibenzoylmethane is treated with bis(benzenesulphonyl)thiodiimide, tetrabenzoylthiiran is obtained,[163] while treatment of 5,5-dimethylcyclohexane-1,3-dione (dimedone) with the same thiodiimide affords compound (I).[164] CH-acids with lower pK_a, for example, malonodinitrile or bis(arenesulphonyl)methanes, do not react with bis(arenesulphonyl)thiodiimides.[163] The reaction of diaroylthiodiimides with acetylacetone, dibenzoylmethane, and dimedone gives rise to 1,3,4-oxathiazole derivatives.[165] It has been suggested[163–165] that *S*-imides are present as intermediates in these reactions:



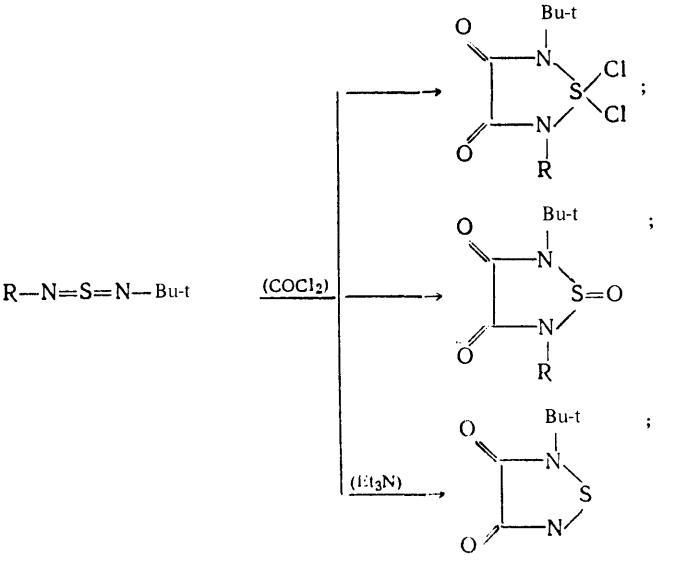
a) R=ArSO$_2$; X=Y=COMe; X=COMe, Y=CO$_2$Et
b) R=ArCO; X=Y=COMe; X=Y=COPh .

11. Other Reactions

Bis(trimethylsilyl)thiodiimide interacts with 4-tolyl- and 4-chlorobenzenesulphenyl chlorides to form the corresponding 1,7-diaryltetrathiotrinitride cations, diaryl disulphide, and molecular nitrogen:[166]



The reaction of thiodiimides with oxalyl chloride in absolute CCl_4 with cooling leads to 1,1-dichloro-2,5-diorganyl-1,2,5-thiadiazolidine-3,4-diones.[167] When the reaction was carried out without cooling, 2,5-diorganyl-3,4-dioxo-1,2,5-thiadiazolidine 1-oxides were obtained, while in the presence of triethylamine the product was 2,5-diorganyl-3,4-dioxo-1,2,5-thiadiazolidines:[168]



R=Ph, t-Bu.

The molecular ions derived from diaryl-, *N*-pentafluorophenyl-*N'*-phenyl-, and bis(pentafluorophenyl)-thiodiimides cyclise according to mass-spectrometric data, losing the *ortho*-substituent in the aromatic ring and forming ions of the benzothiadiazole type with an even number of electrons.[128,169] Diphenylthiodiimide also eliminates sulphur, apparently from the thiadiaziridine isomer of the molecular ion with formation of an azobenzene molecular ion.[128,169] Molecular ions derived from compounds with longer sulphur–nitrogen groups, namely –S–N=S=N– and –S–N=S=N–S–, are fragmented both by the direct cleavage of the sulphur–nitrogen chain and after an intramolecular rearrangement, which leads to the formation of four- and five-membered rings. The contribution of the direct fragmentation increases with increasing length of the sulphur–nitrogen chain. The transition from phenyl derivatives to pentafluorophenyl derivatives has a relatively weak influence on the principal fragmentation reactions, despite the large chemical difference between the C_6H_5 and C_6F_5 groups.[128]

Thus the chemistry of organic compounds containing the thiodiimide group constitute an interesting and developing branch of modern organoelemental chemistry. Further development of this field will probably be associated with the study of compounds containing long acyclic sulphur–nitrogen fragments and also with the synthesis and investigation of the chemical properties of selena- and tellura-analogues of organic thiodiimides, about which little is known at present (see, for example, Refs.121 and 170–172).

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