

## IR AND NMR STUDIES OF SYMMETRICALLY AND UNSYMMETRICALLY BONDED *N,N*-DIALKYLDITHIO-CARBAMATES

BY

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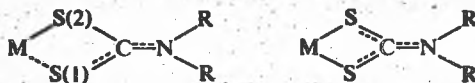
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In order to find characteristic differences between symmetrically and unsymmetrically bonded *N,N*-dialkyldithiocarbamates, their IR and <sup>1</sup>H NMR spectra have been examined. The IR data firmly underline a previously reported infrared criterion which makes it possible to distinguish the two types of bonding. In the spectra of the unsymmetrical *N,N*-diethyldithiocarbamates a band at 1000 cm<sup>-1</sup> is assigned to the C=S stretching mode.

Although the rotation around the S<sub>2</sub>C—NR<sub>2</sub> bond in several dithiocarbamate complexes will be strongly hindered at low temperatures, no splitting of the NMR signals of the *N*-alkyl groups could be observed. This may be attributed to an extremely small difference in magnetic environment of the *N*-alkyl moieties in the rotamers.

### IR-spectra

On the basis of limited data *Bonati* and *Ugo*<sup>1</sup> reported an infrared criterion by which unsymmetrically coordinated *N,N*-diethyldithiocarbamates (Et<sub>2</sub>DTC) could be distinguished from the symmetrical ones (Fig. 1). They found



unsymmetrical      Fig. 1      symmetrical

that the presence of two absorption bands in the region of 1050–950 cm<sup>-1</sup> is characteristic of the unsymmetrically bonded Et<sub>2</sub>DTC groups. For the spectra of the symmetrical Et<sub>2</sub>DTC derivatives only one band is observed in this region.

We have examined the IR-spectra of a series of Et<sub>2</sub>DTC compounds.

<sup>1</sup> F. Bonati and R. Ugo, *J. Organomet. Chem.* **10**, 257 (1967).

It appeared that the spectra of the compounds, the  $\text{Et}_2\text{DTC}$  groups of which are known to be unsymmetrically coordinated, contain the two bands without exception, whereas in the spectra of the bidentate (symmetrical)  $\text{Et}_2\text{DTC}$  complexes only one band is observed (Table I). In Fig. 2 this is illustrated for  $N,N,N',N'$ -tetraethylthiuram disulfide [ $(\text{Et}_2\text{NCSS})_2 = \text{Et}_4\text{TDS}$ ] and the bisdiethyldithiocarbamate complex of  $\text{Zn(II)}$ .

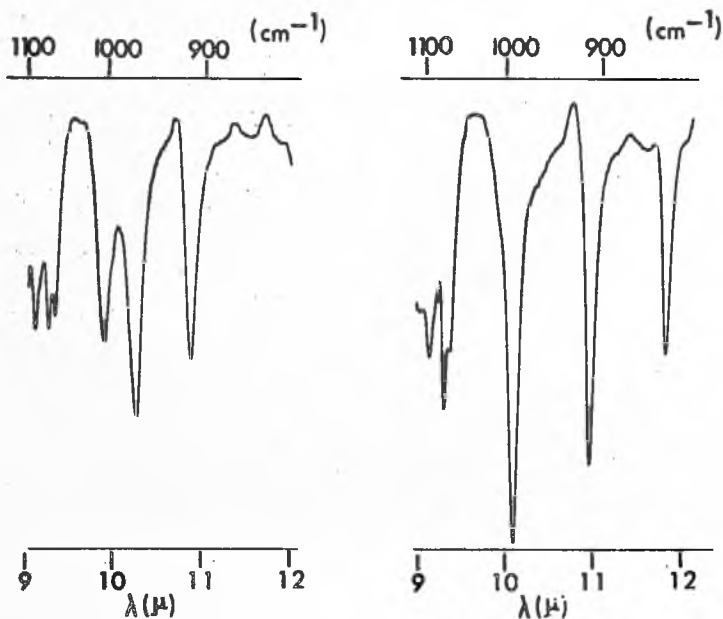


Fig. 2. IR-spectra of  $\text{Et}_4\text{TDS}$  (A) and  $\text{Zn}(\text{Et}_2\text{DTC})_2$  (B) recorded in  $\text{CHCl}_3$ .

These results give a broader basis for the criterion of *Bonati and Ugo*; it is probably of general applicability for DTC complexes. It should be noted that we have considered the data measured in solution rather than those in the solid state. The presence of two bands in the spectra of unsymmetrical  $\text{Et}_2\text{DTC}$  derivatives might be due to splitting of degenerate vibrational states. However, the spectra of symmetrical dithiocarbamates as e.g.,  $\text{Ni}(\text{Et}_2\text{DTC})_2$  ( $\text{D}_{2h}$ ) and  $\text{Cu}(\text{Et}_2\text{DTC})_2$  (in the solid state the symmetry is lower than  $\text{D}_{2h}$ <sup>2</sup>), the symmetries of which do not allow degenerate states for the ligand vibrations, show notwithstanding only one band. So no theoretical foundation for this criterion has been found.

<sup>2</sup> M. Bonamico, G. Dessy, A. Mugnoli, A. Vaciago and L. Zambonelli, *Acta Cryst.* **19**, 886 (1965).

Upon complexation of  $\text{Et}_4\text{TDS}$  to Zn, Cd and  $\text{Hg}^{2+}$  band I shifts to a lower frequency just like the band at  $918\text{ cm}^{-1}$  (band III) which is present in the spectra of all  $\text{Et}_2\text{DTC}$  derivatives investigated. Band III was recently assigned to a CSS vibration on the basis of a comparative IR study of  $\text{Et}_2\text{DTC}$  and *N,N*-diethyldiselenocarbamate ( $\text{Et}_2\text{DSC}$ ) complexes<sup>4</sup>. For band II no significant change could be observed. From the structure of the thiuram disulfide complexes which was indicated previously<sup>5</sup> and confirmed recently by crystallographic work<sup>6</sup>, it follows

Table I  
IR data of  $\text{Et}_2\text{DTC}$  derivatives measured in  $\text{CHCl}_3$ .

Unsymmetrical	Band I $\nu(\text{C}=\text{S}(1))$	Band II	Band III $\nu(\text{CSS})(\text{cm}^{-1})$
$\text{Et}(\text{Et}_2\text{DTC})$	1007 m	990 m	920 m
$\text{Me}(\text{Et}_2\text{DTC})$	1012 m	990 m	919 m
$\text{HgI}_2\text{Me}(\text{Et}_2\text{DTC})^*$	1002 m-w	989 m	909 m
$\text{Et}_4\text{TDS}$	1008 m	972 m	918 m
$\text{HgI}_2(\text{Et}_4\text{TDS})$	1000 m-w	972 m	910 m
$\text{CdI}_2(\text{Et}_4\text{TDS})^*$	992 m-w	971 m	907 m
$\text{ZnI}_2(\text{Et}_4\text{TDS})^*$	991 m-w	971 m	907 m
$\text{As}(\text{Et}_2\text{DTC})_3$	1004 m-w	988 m	915 m
$\text{Sb}(\text{Et}_2\text{DTC})_3$	1000 sh	988 m	915 m
$\text{Bi}(\text{Et}_2\text{DTC})_3$	1000 sh	985 m	913 m
$\text{Se}(\text{Et}_2\text{DTC})_2$	1005 m	983 m	915 m
$\text{Te}(\text{Et}_2\text{DTC})_2$	1002 m	986 m	916 m
$\text{Sn}(\text{Et}_2\text{DTC})_4^7$	1000 sh	991 m	917 m
symmetrical			
$\text{Co}(\text{Et}_2\text{DTC})_3$	1005 m-w		918 m-w
$\text{Zn}(\text{Et}_2\text{DTC})_2$	991 m		914 m
$\text{Hg}(\text{Et}_2\text{DTC})_2$	989 m		913 m
$\text{Ni}(\text{Et}_2\text{DTC})_2^8$	993 m		914 m
$\text{Ni}(\text{Et}_2\text{DTC})_3 \cdot \text{I}_3^{-*3}$	998 m-w		913 w
$\text{Cu}(\text{Et}_2\text{DTC})_2^9$	998 m		915 m

\* The spectra were recorded in KBr. The accuracy of the data given is  $\pm 2\text{ cm}^{-1}$ ; as reference the band at  $1028\text{ cm}^{-1}$  of polystyrene was used, m = moderate intensity, w = weak intensity, sh = shoulder

<sup>2</sup> H. C. Brinkhoff, J. A. Cras, J. J. Steggerda and J. Willemsse, *Rec. Trav. Chim.* 88, 633 (1969).

<sup>4</sup> A. T. Pilipenko and N. V. Mel'nikova, *Russ. J. of Inorg. Chem.* 14, 236 (1969).

<sup>5</sup> H. C. Brinkhoff, A. M. Grotens and J. J. Steggerda, *Rec. Trav. Chim.* 89, 11 (1970).

<sup>6</sup> P. T. Beurskens, J. A. Cras, J. H. Noordik and A. M. Spruijt, *J. of Crystal and Molecular Structure*, 1, 93 (1971).

<sup>7</sup> F. Bonati, G. Minghetti and S. Cenini, *Inorg. Chim. Acta* 2, 375 (1968).

that the  $C=S[C=S(1)]$  bond lengths become longer upon complex formation. This weakening of the  $C=S$  bond correlated with the shift of band I to lower frequency leads to the assignment of this band to a vibrational mode wherein the contribution of the  $C=S$  stretching vibration is important. To verify this assignment a new complex  $HgI_2Me(Et_2DTC)$  was prepared simply by adding equimolar amounts of  $HgI_2$  and  $MeS(S)CNEt_2$  in acetone solution.

The  $Et_2DTC$  ester will complex mainly by means of the terminal sulfur atom  $[S(1)]$  like the  $R_4TDS$  ligands. The shift of the bands I and III to lower frequencies upon complexation gives support to our assignment of band I.

### $^1H$ NMR-spectra

It was reported that hindered rotation around the  $C-N$  bond can be observed by  $^1H$  NMR for unsymmetrical  $R_2DTC$  derivatives like  $R_2DTC$  esters<sup>8,9</sup>,  $R_4TDS$  and its complexes<sup>5</sup>. Hindered rotation for symmetrical  $R_2DTC$  derivatives in general cannot be observed by NMR. The compounds  $Mo(NO)(R_2DTC)_3$  and  $Ru(NO)(R_2DTC)_3$ , which were studied by *Johnson, Al-Obaidi* and *McCleverty*<sup>10,11</sup>, form an exception. This is caused by the non-equivalence of the  $N$ -alkyl groups with respect to the other ligands coordinated to the central atom. We have studied some unsymmetrical  $R_2DTC$  compounds in order to check if they could be distinguished from the symmetrical ones by NMR. For the compounds investigated only hindered rotation around the  $C-N$  bond is observed in  $N,N,N',N'$ -tetramethylthiuram monosulfide ( $Me_4TMS$ ) which shows two singlets of equal intensity in its NMR-spectrum recorded at  $30^\circ$  in  $CDCl_3$  solution with a spectrometer operating at 100 MHz. The splitting between the signals is 7 Hz. For  $As(Et_2DTC)_3$ , its  $Sb$  and  $Bi$  analogues,  $As(Me_2DTC)_3$ ,  $Se(Et_2DTC)_2$  and  $Te(Et_2DTC)_2$ , however, no splitting of the  $N$ -alkyl proton resonances in  $CDCl_3$  and  $CS_2$  solutions could be observed at temperatures as low as  $-60^\circ$ . Even a spectrum of  $As(Et_2DTC)_3$ , recorded with a 220 MHz NMR spectrometer at  $-50^\circ$  in a  $CS_2$ -toluene solution, shows no line broadening of the ethyl proton resonance peaks with respect to the  $CH_3$ -signal of toluene. This might be due either to a small, undetectable difference in the magnetic environments of the  $N$ -alkyl groups in the rotamers or to a small barrier to internal rotation. The former is sometimes found, de-

<sup>8</sup> a. *C. E. Holloway* and *M. H. Gitlitz*, *Can. J. Chem.*, **45**, 2659 (1967);

b. *A. E. Lemire* and *J. C. Thompson*, *ibid.* **48**, 824 (1970).

<sup>9</sup> *J. L. Richards*, *D. S. Tarbell* and *E. H. Hoffmeister*, *Tetrahedron*, **4**, 6485 (1968).

<sup>10</sup> *B. F. G. Johnson* and *K. H. Al-Obaidi*, *Chem. Comm.* 876 (1968).

<sup>11</sup> *B. F. G. Johnson*, *K. H. Al-Obaidi* and *J. A. McCleverty*, *J. Chem. Soc. A*, 1668 (1969).

pending upon solvent, for the  $N\text{-CH}_3$  protons of some alkyl- $N$ -(arenesulfonylmethyl)- $N$ -methylcarbamates ( $\text{XC}_6\text{H}_4\text{SO}_2\text{CH}_2\text{N}(\text{CH}_3)\text{CO}_2\text{R}$ )<sup>12,13</sup>.

From the small differences in the  $\text{C}\cdots\text{N}$  bond length found for  $\text{Et}_4\text{TDS}$ <sup>14</sup> and  $\text{As}(\text{Et}_2\text{DTC})_3$ <sup>15</sup> and the slight variations in the  $\text{C}\cdots\text{N}$  stretching frequencies of the complexes investigated,  $\text{R}_4\text{TDS}$  and  $\text{R}'(\text{R}_2\text{DTC})$  (Table II), it is concluded that the first explanation (valid at the temperatures mentioned) is most probably correct.

### Experimental Part

<sup>1</sup>H NMR spectra were recorded using a Varian HA-100 NMR spectrometer operating at 100 MHz. For recording the 220 MHz <sup>1</sup>H NMR spectrum the Varian AR 220 MHz NMR spectrometer was used. The infrared data were obtained, unless reported otherwise,

Table II

The  $\text{C}\cdots\text{N}$  stretching frequencies of a number of  $\text{Me}_2\text{DTC}$  and  $\text{Et}_2\text{DTC}$  derivatives; crystallographic data of the  $\text{C}\cdots\text{N}$  bond lengths.

	$\nu(\text{C}\cdots\text{N})(\text{cm}^{-1})$	$\text{C}\cdots\text{N}(\text{\AA})$
$\text{Me}_4\text{TDS}$	1505	1.31 <sup>16</sup>
$\text{Me}_4\text{TMS}$	1508	
$\text{Me}(\text{Me}_2\text{DTC})$	1498**	
$\text{Et}(\text{Me}_2\text{DTC})$	1498**	
$\text{As}(\text{Me}_2\text{DTC})_3$	1507	
$\text{Me}(\text{Et}_2\text{DTC})$	1493	
$\text{Me}(\text{Et}_2\text{DTC})$	1489**	
$\text{Et}(\text{Et}_2\text{DTC})$	1493	
$\text{Et}(\text{Et}_2\text{DTC})$	1489**	
$\text{Et}_4\text{TDS}$	1496	1.35 <sup>14</sup>
$\text{As}(\text{Et}_2\text{DTC})_3$	1494	1.34 <sup>15</sup>
$\text{Se}(\text{Et}_2\text{DTC})_2$	1497	
$\text{Te}(\text{Et}_2\text{DTC})_2$	1493	

The spectra were recorded in  $\text{CHCl}_3$  solution, using a Beckmann IR 4 spectrophotometer.

\* The spectra were recorded in  $\text{CH}_2\text{Cl}_2$  solution.

<sup>12</sup> S. van der Werf, Thesis, Groningen 1969, pg 50 and 51.

<sup>13</sup> S. van der Werf and J. B. F. N. Engberts, Tetrahedron Letters 29, 3311 (1968).

<sup>14</sup> I. L. Karle, J. A. Estlin and K. Britts, Acta Cryst. 22, 273 (1967).

<sup>15</sup> M. Colapietro, A. Domenicano, L. Scaramuzza and A. Vacicigo, Chem. Comm. 302 (1968).

<sup>16</sup> K. Marøy, Acta Chem. Scand. 19, 509 (1965).

using a Perkin Elmer 157. The known compounds were prepared as described in the literature:  $\text{Me}_4\text{TMS}^{17}$ ,  $\text{As}(\text{Et}_2\text{DTC})_3$ ,  $\text{Sb}(\text{Et}_2\text{DTC})_3$ ,  $\text{Bi}(\text{Et}_2\text{DTC})_3$ ,  $\text{Se}(\text{Et}_2\text{DTC})_2$ ,  $\text{Te}(\text{Et}_2\text{DTC})_2$ ,  $\text{Et}(\text{Et}_2\text{DTC})$ ,  $\text{Me}(\text{Et}_2\text{DTC})$ ,  $\text{Co}(\text{Et}_2\text{DTC})_3$ ,  $\text{Zn}(\text{Et}_2\text{DTC})_2$ ,  $\text{Hg}(\text{Et}_2\text{DTC})_2$ ,  $\text{Cu}(\text{Et}_2\text{DTC})_2$ ,  $\text{Ni}(\text{Et}_2\text{DTC})_2$ ,  $\text{Me}_4\text{TDS}$ ,  $\text{Et}_4\text{TDS}^{18}$  and  $\text{Sn}(\text{Et}_2\text{DTC})_4^7$ . The preparation of the thiuram disulfide complexes and  $\text{Ni}(\text{Et}_2\text{DTC})_3^+ \cdot \text{I}_3^-$  was as described in ref. 3. The synthesis of  $\text{HgI}_2(\text{Et}_4\text{TDS})$  was reported earlier<sup>5</sup>.

$\text{CdI}_2(\text{Et}_4\text{TDS})$ . A concentrated solution of  $\text{I}_2$  (1 mole) in  $\text{CS}_2$  was added to a concentrated solution of  $\text{Cd}(\text{Et}_2\text{DTC})_2^{19}$  in the same solvent. The white precipitate obtained was dissolved in acetone and reprecipitated by addition of petroleum ether (60–80°). The colourless needles melted at 139–142°.

Found : Cd 16.9; C 18.3; H 3.0  
Calc. for  $\text{CdI}_2 \cdot \text{C}_{10}\text{H}_{20}\text{N}_2\text{S}_4$  (662.7): Cd 17.0; C 18.1; H 3.0

$\text{ZnI}_2(\text{Et}_4\text{TDS})$  was obtained like  $\text{CdI}_2(\text{Et}_4\text{TDS})$ . Instead of acetone, chloroform was used for recrystallisation. Colourless needles were formed; m.p. 153–156°.

Found : Zn 10.6; C 19.7; H 3.3.  
Calc. for  $\text{ZnI}_2 \cdot \text{C}_{10}\text{H}_{20}\text{N}_2\text{S}_4$  (615.7): Zn 10.6; C 19.5; H 3.3.

$\text{Ni}(\text{Et}_2\text{DTC})_3\text{I}_2$ . An excess of iodine was added to a solution of  $\text{Ni}(\text{Et}_2\text{DTC})_2$  in chloroform. The separated oil solidified on addition of petroleum ether (60–80°). Recrystallisation in acetone solution yielded needles which melted at 121–123°.

Found : Ni 6.5; C 20.7; H 3.5.  
Calc. for  $\text{NiI}_3 \cdot \text{C}_{15}\text{H}_{30}\text{N}_3\text{S}_6$  (884.2): Ni 6.6; C 20.4; H 3.4.

$\text{HgI}_2\text{Me}(\text{Et}_2\text{DTC})$ .  $\text{HgI}_2$  (1 mole) was added to a concentrated solution of  $\text{Me}(\text{Et}_2\text{DTC})$  (1 mole) in acetone. After the  $\text{HgI}_2$  had dissolved by complexation with the ester, light yellow plates were obtained on addition of petroleum ether (60–80°); m.p. 101–103°.

Found : C 12.0; H 2.2.  
Calc. for  $\text{HgI}_2 \cdot \text{C}_6\text{H}_{13}\text{NS}_2$  (617.7): C 11.7; H 2.1.

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<sup>17</sup> *J. v. Braun* and *F. Stechele*, Ber, 36, 2275 (1903).

<sup>18</sup> *G. D. Thorn* and *R. A. Ludwig*, The Dithiocarbamates and related compounds, Elsevier, Amsterdam, 1962.