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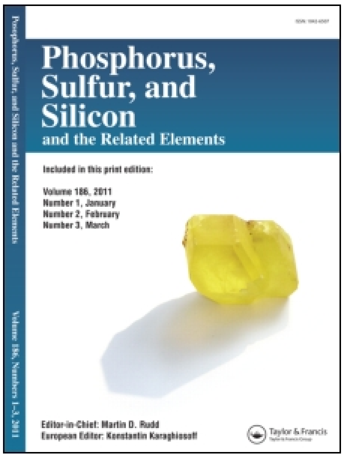

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
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CONFORMATION AND C—N ROTATIONAL BARRIER OF DITHIOCARBAMATE ESTERS-NMR AND MOLECULAR ORBITAL STUDIES

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To cite this Article Devi, K. R. Gayathri , Manogaran, S. and Sathyanarayana, D. N.(1981) 'CONFORMATION AND C—N ROTATIONAL BARRIER OF DITHIOCARBAMATE ESTERS-NMR AND MOLECULAR ORBITAL STUDIES', Phosphorus, Sulfur, and Silicon and the Related Elements, 11: 1, 47 — 54

To link to this Article: DOI: 10.1080/03086648108077402

URL: http://dx.doi.org/10.1080/03086648108077402

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Phosphorus and Sulfur, 1981, Vol. 11, pp. 47–54
0308-664X/81/1101-0047/$06.50/0

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CONFORMATION AND C—N ROTATIONAL BARRIER OF DITHIOCARBAMATE ESTERS-NMR AND MOLECULAR ORBITAL STUDIES

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(*Recieved July 14, 1980; in final form January 5, 1981*)

The variable temperature proton and ambient temperature carbon-13 NMR spectra of S-methyl dithiocarbamate esters have been recorded. The results of the theoretical energy calculations (CNDO/2 and EHT types) together with the experimental data have been interpreted in terms of the molecular conformations. The barrier heights for the rotation about the thioamide C—N bond are calculated using the CNDO/2 method and the results are discussed in terms of the computed charge densities and bond orders.

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INTRODUCTION

Over the years, interest in the molecular conformations of carboxylic esters has steadily increased.[1,2] Relatively little spectroscopic work has been carried out on the conformation of sulfur esters. A common category of sulfur esters is dithioesters (R″ CSSR′), of which dithiocarbamate esters (R″ = NR_2) form an important class owing to the importance of alkyl dithiocarbamates in industrial and biological processes.[3]

The aim of the present work is to study the conformational preferences of dithiocarbamate esters: S-methyl dithiocarbamate (SMDTC), S-methyl N-methyl dithiocarbamate (MMDTC) and S-methyl N,N-dimethyl dithiocarbamate (MDMDTC), by means of variable temperature proton NMR spectroscopy and theoretically by the all valence CNDO/2 and EHT methods. The ^{13}C NMR spectra have also been obtained. The results are correlated and discussed. Save for the barrier height measurements by proton NMR method of MDMDTC,[4] no work is reported on barrier heights in dithiocarbamate esters. The barrier heights for the rotation about the thioamide C—N bond are therefore calculated using the CNDO/2 method and compared with the experimental values wherever available.

THEORETICAL TREATMENT

The all valence CNDO/2 molecular orbital calculations were carried out in the original form and parametrization.[5] The EHT method using the Wolfsberg-Helmholtz procedure of evaluation for the off-diagonal elements was employed.[6] A full basis set of valence atomic orbitals including the 3d orbitals of sulfur has been considered in the calculations. The geometries for the DTC esters were constructed from the molecular parameters available for dithiocarbamates[3,7] and dimethyldisulphide.[8]

TABLE I

Molecular Parameters of Dithiocarbamate Esters

Bond distance (nm)		Bond angle (deg)	
C=S	0.170	SCS	122.0
C—S	0.178	NCS	124.0
C′—S	0.181	CSC	100.0
C—N	0.133	HC′S	109.47
C″—N	0.147	HC′H	109.47
N—H	0.101	CNH	120.0
C—H	0.108	HNC″	120.0
		CNC	120.0
		NCH	109.47
		HC″H	109.47

C′: S-methyl carbon, C″: N-methyl carbon.

The bond lengths and bond angles compiled in Table I were assumed to be constant during the internal rotation.

The computations were made on a DEC 1090 computer. For the CNDO/2 method, the QCPE program[9] was employed. Program in Fortran IV was written for the EHT calculations.

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RESULTS AND DISCUSSION

The dithiocarbamate esters may be predicted to possess appreciable barrier heights about the C—N bond as in related alkyl thionamides.[10] In addition these esters may also possess very low barrier heights about the ester C—S bond. The following planar conformations may be written for the dithiocarbamate esters. The symbolism *cis* and *trans* refers to the orientation of the alkyl groups with respect to the C=S group.

A planar molecular arrangement would best enable the ester sulfur atom to share its lone-pair with the pi orbital system and thus resulting in extra stabilization. The results of the NMR studies are in good agreement with the M.O calculations as discussed below.

PROTON NMR SPECTRA

SMDTC. At temperatures below 273 K, two signals, a very intense signal at 2.55 ppm and a very weak one at 2.08 ppm are observed in the proton NMR spectrum of SMDTC assignable to the *trans* (Ib) and *cis* (Ia) (S)CH_3 protons. The *cis* isomer was estimated to be about 7 percent at 233 K from the relative peak intensities. At room temperature only the highfield signal is observed, suggesting that the *trans* conformer of SMDTC exists predominantly in solution. The NMR spectrum of SMDTC also displays two broad bands corresponding to the NH_2 protons centered at 7.04 and 7.89 ppm at 273 K. The doublet arises from the differently shielded *cis* and *trans* NH protons due to restricted rotation about the C—N bond. At lower temperatures the bands sharpen.

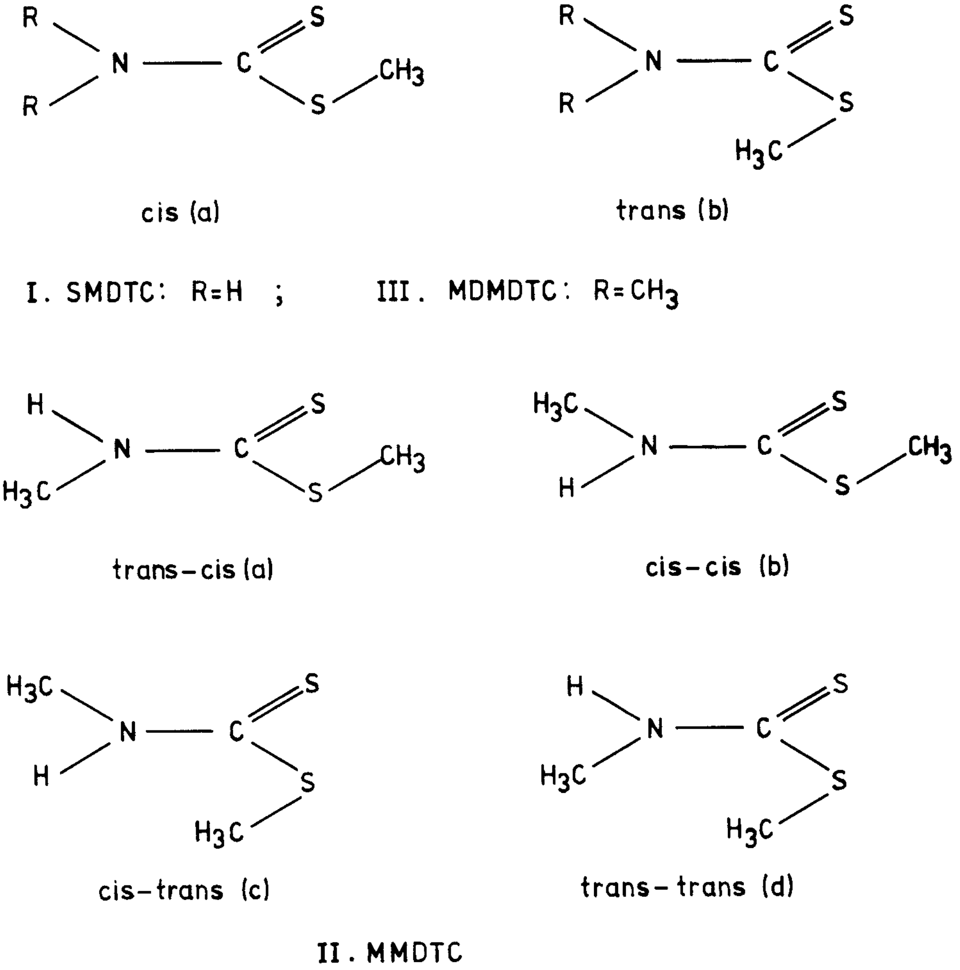

FIGURE 1 Conformations of dithiocarbamate esters.

MMDTC The spectrum of MMDTC at 283 K displays two signals at 2.62 and 2.67 ppm corresponding to (S)CH_3 protons. The intensity of the 2.62 ppm signal is much higher than that of the 2.67 ppm signal. The latter peak, the intensity of which increases with lowering of temperature, may be assigned to the *trans* isomer. From the relative peak intensities the *trans* form is estimated to be 30 percent at 273 K and 40 percent at 233 K. Similar results have been reported in the literature for secondary carbamates and thiocarbonates.[2,11]

The NMR spectrum of MMDTC at room temperature exhibits additionally two more peaks centered at 3.25 and 3.08 ppm, each of which is a doublet due to the spin-spin coupling between (N)CH_3 and NH protons ($J = 5$ Hz), attributable respectively to the less and more shielded *trans* and *cis* (N)CH_3 protons.[10] As estimated from the integrated signal intensities, the *trans* N—CH_3 isomer is present in equilibrium with the *cis* isomer in the ratio of ~3:1 at 293 K and in the ratio of ~3:2 at 233 K. Similar findings have been reported for monothiocarbamate from NMR

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investigations.[12] However for the analogous oxygen compound only the *cis* N—CH_3 isomer is said to be stable at ambient temperature.[11] Likewise, in several secondary amides, ureas and their thioanalogues, the *cis* conformer (NH *trans* to C = O/S) has been shown to occur predominantly by different physical measurements.[10] Further, as is to be expected, two broad weak signals at 7.85 and 8.60 ppm at ambient temperature attributable to the NH protons of the two rotomers are observed in the spectrum of MMDTC.

MDMDTC. The NMR spectrum of MDMDTC shows only one peak at 2.60 ppm corresponding to *cis* (S)CH_3 protons (IIIa). This signal is unaffected at subambient temperatures indicating that only one conformation is accessible for MDMDTC. Further, separate signals at 3.39 and 3.60 ppm in the intensity ratio of 1:1 arising from *cis* and *trans* (N)CH_3 protons are found. The greater stability of the *cis* isomer over the *trans* form (IIIb) is attributable to the steric hindrance between (N)CH_3 and (S)CH_3 groups in the *trans* form.

CARBON-13 NMR SPECTRA

The ^{13}C NMR spectroscopy has been successfully utilised for the study of molecular conformations in solution.[13] This in general requires the analysis of the spectra at several temperatures. In the present study, the spectra at ambient temperature are only recorded, however. The thiocarbonyl carbon resonance measured downfield from internal TMS of DTC esters shows gradual variation from SMDTC (203.8 ppm), to MMDTC (199.5 ppm) to MDMDTC (198.6 ppm). The signal arising from the (S)CH_3 carbon is observed near 20.0 ppm (SMDTC 19.6; MMDTC 18.3; MDMDTC 20.5 ppm).

In the spectrum of MMDTC, there are two signals, an intense one at 33.95 ppm and a weak one at 32.74 ppm. These signals may be attributed to originate from the *trans-cis* and *cis-cis* rotomers of MMDTC. This is concordant with the ^1H NMR spectral results. Further, the spectrum of MDMDTC has resonances at 40.8 and 42.3 ppm corresponding to the *trans* and *cis* (N)CH_3 carbons, respectively. The chemical shift difference (1.21) between the *trans* and *cis* (N)CH_3 carbons of MMDTC is compatible with that in MDMDTC (1.5).

MOLECULAR ORBITAL STUDIES

The results of the molecular orbital calculations are found in Table II. The magnitude of the total energy differences for the conformations by the EHT method differs significantly from that by the CNDO/2 method, the trend being the same in both, however. From the table it is clear that the results for MMDTC and MDMDTC are in excellent agreement with the qualitative conclusions from the NMR spectra. The results rule out the existence of *trans-trans* (IId) form for MMDTC and the *trans* (IIIb) form for MDMDTC. However, for SMDTC the results are contradictory. This may be attributed to the limitations of the theoretical methods employed. The preference for one or the other form could be affected by factors such as intermolecular interactions with the solvent which are not considered in the calculations. Therefore, as also derived from the NMR spectra, two conformations are accessible for SMDTC and three for MMDTC while MDMDTC exists solely as one conformer.

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TABLE II

Calculated Conformational Stabilities of Dithiocarbamate Esters

Compound	Conformer	Total molecular energy difference† (kcal mol^{-1}) CNDO/2	EHT
SMDTC	*cis*		
	trans (stag. CH$_3$)	4.9	
	trans (ecl. CH$_3$)	21.4	11.5
NMDTC	*trans-cis*		
	cis-cis	7.6	0.5
	cis-trans	12.4	1.0
	trans-trans	3.2×10^4	37.7
MDMDTC	*cis*		
	trans	3.2×10^4	86.75

† Difference from the stablest conformation.

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TABLE III

The Variation of Total Energies (kcal mol^{-1}) as Function of Angle of Twist θ

			Energy		
Angle of Twist θ		SMDTC		MMDTC	MDMDTC (*cis*)
	cis (Ia)	*Trans* (CH$_3$ stag)	*Trans* (CH$_3$ eclipsed)		
0	0.0	0.0	0.0	0.0	0.0
30	5.19	5.42	−1.64	9.70	10.30
60	17.02	17.27	4.84	25.24	26.38
90	24.23	24.32	10.68	32.77	33.48
120	17.02	17.27	4.84	25.99	26.04
150	5.19	5.42	−1.64	13.49	10.84
180	0.0	0.0	0.0	7.62	3.42

ROTATIONAL BARRIERS

A planar dithiocarbamate skeleton was assumed in view of the results on similar molecules.[14] The results discussed later clearly support that the dithiocarbamate molecular skeleton is planar. Furthermore, a staggered conformation of the methyl groups was used for MDMDTC to minimize the computational work. Similarly for MMDTC the N—CH$_3$ group staggered with respect to NH was considered. The barrier height calculation for SMDTC has been performed for both conformations Ia and Ib, and for the latter conformation, the calculations have been extended to both staggered and eclipsed forms of the S—CH$_3$ group. In the actual molecules the CH$_3$ groups rotate to minimize the energy both in the ground and in the transition states. Since the CNDO/2 method is not ideally suited to handle steric effects, a rigid model has been preferred, however.

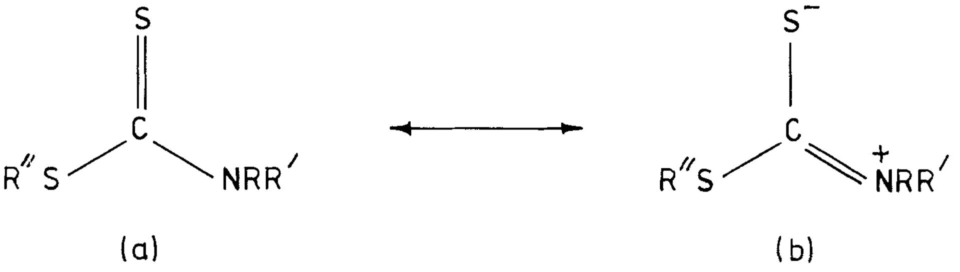

FIGURE 2 Resonance structures.

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The total molecular energy was calculated as a function of the rotational parameter θ describing the rotation about the C—N bond at 30° intervals. These angles are measured in the clockwise direction from the planar conformation shown in Figure 1. The results are collected in Table III. The energy difference (ΔE) between the energy calculated for the initial state ($\theta = 0°$) and that for the transition state ($\theta = 90°$) was taken as a measure of the barrier height. In support of this assumption, energy maxima are found for $\theta = 90°$.

The barrier to rotation about the C—N bond depends on the pi-stabilization in the ground state. The contribution of (b) to the resonance hybrid (Figure 2) should raise the barrier. The N-methyl group acts as a strong electron releasing moiety forcing sulfur to accept electrons. This stabilizes the resonance structure (b) resulting in the increased barrier height. The higher the barrier more electrons are donated to the thiocarbonyl carbon and consequently a more positive pi charge on terminal sulfur is accumulated. The charge densities vary from SMDTC to MDMDTC in accord with this prediction (Figure 3). As a consequence of this the ^{13}C resonance of the thiocarbonyl carbon shifts to high field in the sequence SMDTC < MMDTC < MDMDTC. The computed C—N bond orders (Figure 3) show the expected variation: increasing N-methylation increases the C—N bond order with concomittant decrease in the C—S bond order, Further, the calculated barriers for the C—N bond vary in an expected manner from SMDTC to MDMDTC. It should be noted that the experimental barrier heights as determined by the NMR method[4,15] (10.3–11.5 kcal/mol) are somewhat lower than those calculated (Table III). Similar findings have been made in the literature.[16] It should be noted that the experimental values refer to barriers measured in solution while calculated barriers correspond to gas-phase values. In addition, in the calculations, no account has been taken for the variation of the geometries around the C—N bond in the transition state.

It is of interest to compare the C=S and C—N bond orders of MDMDTC with those of dimethyldithiocarbamate ion (DMDTC) to note the effect of S-methylation. The pi bond orders of the C—N and C—S of DMDTC ion are 0.508 and 0.528 respectively.[17] Upon S-methylation, the C—S bond order at which methylation takes place has a lower bond order (0.277) while the bond order of the other C—S group increases (0.661). The C—N bond order also shows an increase (0.570). The calculated pi bond orders are thus in accord with the qualitative predictions.

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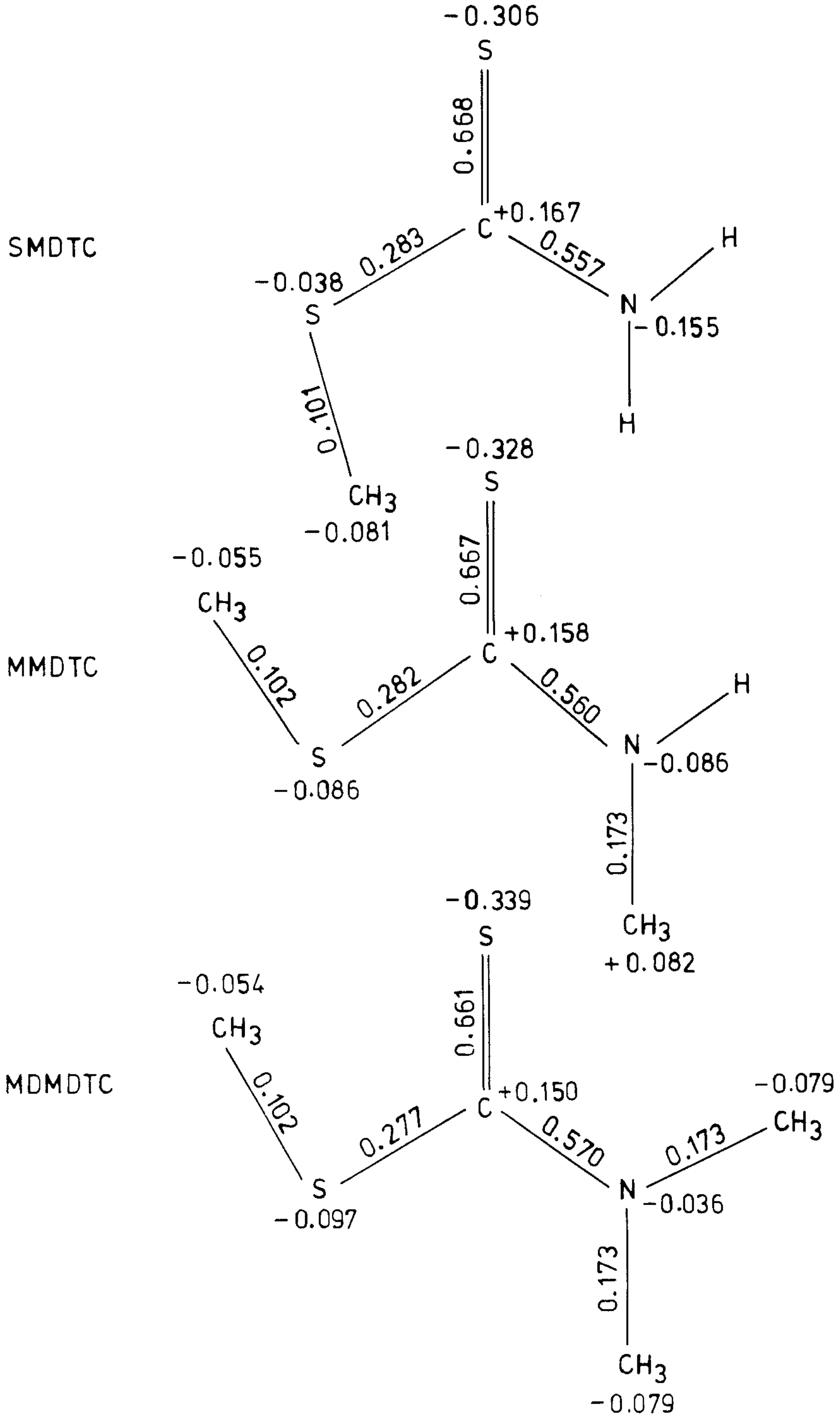

FIGURE 3 Calculated pi bond orders and charge densities for dithiocarbamate esters.

EXPERIMENTAL

The esters were synthesised and purified according to literature methods.[18] The identity of the compounds was established by physical constants and chemical analysis.

The variable temperature proton NMR spectra were recorded with a Bruker WH 270 MHz Fourier transform spectrometer between 233 to 313 K at 10° interval. $CDCl_3$ was used as solvent and TMS as the internal calibrant. The carbon-13 NMR spectra were obtained at ambient temperature (293 K) using the same instrument operating at 67.89 MHz under conditions of complete proton noise decoupling as well as off-resonance decoupling. Samples were dissolved in $CDCl_3$ containing 2 percent TMS.

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