

Theoretical Study of the Most Stable Conformations of *NN'*-Dimethylthiourea, *NNN'*-Trimethylthiourea, and the Methyl Ester of Dithiocarbazic Acid

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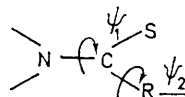
CNDO/2 Calculations on *NN'*-dimethylthiourea, *NNN'*-trimethylthiourea, and the methyl ester of dithiocarbazic acid are reported. The results are in satisfactory agreement with experimental data (n.m.r. spectra) on the equilibrium conformations found in solutions of these systems.

SULPHUR-CONTAINING molecules are becoming more and more important in the chemistry of co-ordination compounds since they form S-bonded complexes with various metal cations. Amongst these molecules, *N*-alkyl substituted thioureas have been extensively studied by means of several techniques (*X*-ray analysis, electronic, vibrational, and n.m.r. spectroscopy, etc.).¹⁻²⁸ More recently derivatives of dithiocarbazic acid have aroused the interest of several research groups and a number of papers dealing with their synthesis, and preparation, characterization, and spectral properties of their complexes have appeared.²⁹⁻³⁴ One of the problems to be solved concerns determination of the most stable conformations of the free ligand and the possibility of an equilibrium between two or more different conformations. This problem appears to be of great importance in intramolecular hydrogen bonding in some metal complexes where this type of interaction is only compatible with some particular conformation of the ligand. In previous papers^{27,28} the possibility of co-ordinated trimethylthiourea (tmtu) giving rise to intramolecular hydrogen bonds has been discussed. In connection with these and related papers, an in-

vestigation of the ability of theoretical methods to give information about the most stable conformations of systems of this type was of interest.

RESULTS AND DISCUSSION

Quantum-mechanical techniques have been recently used in an investigation of conformational flexibility and the barrier to internal rotation^{35,36} in molecules very similar to those we are interested in here. The methods employed were semi-empirical, especially CNDO/2³⁷ and EHT.³⁸ In this paper we present results obtained with CNDO/2 on *NNN'*-trimethylthiourea (tmtu), *NN'*-dimethylthiourea (dmtu), and *S*-methyl esters of dithiocarbazic acid (dtca), monothiocarbazic acid, and 2-methyldithiocarbazic acid.



(I)

All the molecules investigated can be referred to the general formula (I) and a complete analysis would

¹ R. L. Carlin and S. L. Holt, jun., *Inorg. Chem.*, 1963, **2**, 849.

² F. A. Cotton, O. D. Faut, and J. T. Mague, *Inorg. Chem.*, 1964, **3**, 17.

³ S. L. Holt, jun., and R. L. Carlin, *J. Amer. Chem. Soc.*, 1964, **86**, 3017.

⁴ C. T. Flint and M. Goodgame, *J. Chem. Soc. (A)*, 1966, 744.

⁵ M. Schafer and C. Curran, *Inorg. Chem.*, 1966, **5**, 265.

⁶ C. Puglisi and R. Levitus, *J. Inorg. Nuclear Chem.*, 1967, **29**, 1069.

⁷ E. Cervone, P. Cancellieri, and C. Furlani, *J. Inorg. Nuclear Chem.*, 1968, **30**, 2431.

⁸ T. Tarantelli and C. Furlani, *J. Chem. Soc. (A)*, 1968, 1717; *Gazzetta*, 1970, **100**, 1012; *ibid.*, p. 1076.

⁹ O. Piovesana and C. Furlani, *J. Inorg. Nuclear Chem.*, 1968, **30**, 1249.

¹⁰ O. Piovesana and C. Furlani, *J. Inorg. Nuclear Chem.*, 1970, **32**, 879.

¹¹ T. J. Lane, A. Yamaguchi, J. V. Quagliano, J. A. Ryan, and S. Mizushima, *J. Amer. Chem. Soc.*, 1959, **81**, 3824.

¹² R. A. Bailey and T. R. Peterson, *Canad. J. Chem.*, 1968, **46**, 3119.

¹³ R. K. Gosavi, U. Agarwala, and C. N. R. Rao, *J. Amer. Chem. Soc.*, 1967, **89**, 235.

¹⁴ A. V. Malik, *J. Inorg. Nuclear Chem.*, 1970, **32**, 1743.

¹⁵ H. Luth and M. R. Truter, *J. Chem. Soc. (A)*, 1968, 1879.

¹⁶ N. R. Kunchur and M. R. Truter, *J. Chem. Soc.*, 1958, 3478.

¹⁷ M. Nardelli, L. Cavalca, and A. Braibanti, *Gazzetta*, 1957, **87**, 138.

¹⁸ A. Lopez-Castro and M. R. Truter, *J. Chem. Soc.*, 1963, 1309.

¹⁹ W. T. Robinson, S. L. Holland, and G. B. Carpenter, *Inorg. Chem.*, 1967, **6**, 605.

²⁰ L. Cavalca, P. Domiano, A. Musatti, and P. Sgarabotto, *Chem. Comm.*, 1968, 1136.

²¹ M. Nardelli, I. Chierici, and A. Braibanti, *Gazzetta*, 1958, **88**, 37.

²² M. Nardelli and I. Chierici, *Ricerca sci.*, 1959, **29**, 1733.

²³ M. Bonamico, G. Dessy, V. Fares, and L. Scaramuzza, *J. Chem. Soc. (A)*, 1971, 3195.

²⁴ A. M. Giuliani, *J.C.S. Dalton*, 1972, 493.

²⁵ A. M. Giuliani, *J.C.S. Dalton*, 1972, 497.

²⁶ D. R. Eaton and K. Zaw, *Canad. J. Chem.*, 1971, **49**, 3315.

²⁷ D. Gattegno and A. M. Giuliani, *J.C.S. Dalton*, 1973, 1646.

²⁸ D. Gattegno, A. M. Giuliani, M. Bossa, and G. Ramunni, *J.C.S. Dalton*, 1973, 1399.

²⁹ U. Anthoni, *Acta Chem. Scand.*, 1966, **20**, 2742.

³⁰ C. Battistoni, G. Mattogno, A. Monaci, and F. Tarli, *J. Inorg. Nuclear Chem.*, 1971, **33**, 3815; *Inorg. Nuclear Chem. Letters*, 1971, **7**, 1081; *ibid.*, p. 981; *Proc. 13th Internat. Conf. Co-ordination Chem.*, 1970, **1**, 269.

³¹ K. A. Jensen, U. Anthoni, and A. Holm, *Acta Chem. Scand.*, 1969, **23**, 1916.

³² P. V. Gogorishvili and M. G. Tskitishvili, *Russ. J. Inorg. Chem.*, 1962, **7**, 649.

³³ M. Akbar Ali, S. E. Livingstone, and D. J. Phillips (a) *Inorg. Chim. Acta*, 1971, **5**, 119; (b) *ibid.*, p. 493; (c) *ibid.*, 1972, **6**, 11; (d) *ibid.*, p. 39.

³⁴ C. Battistoni, M. Bossa, C. Furlani, and G. Mattogno, *J. Electron Spectroscopy*, accepted for publication.

³⁵ C. N. R. Rao, K. Gurudath Rao, Abba Goel, and D. Balasubramanian, *J. Chem. Soc. (A)*, 1971, 3077.

³⁶ J. F. Yan, F. A. Momamy, R. Hoffmann, and H. A. Scheraga, *J. Phys. Chem.*, 1970, **74**, 420.

³⁷ J. A. Pople and G. A. Segal, *J. Chem. Phys.*, 1966, **44**, 3289.

³⁸ R. Hoffmann, *J. Chem. Phys.*, 1963, **39**, 1397.

involve independent variation of ψ_1 and ψ_2 leading to a two dimensional energy map. We instead obtained only slices of the latter, by fixing one of the rotational angles and calculating the energy for different values of the other angle. All calculations were performed on the I108 UNIVAC computer of the Centro di Calcolo, Rome University, by means of a program kindly supplied by the QCPE organization.³⁹ The method of calculation was the usual one, as given by Pople.³⁷ A list of the parameters used is given in Table 1. Bond

TABLE 1

Parameters used in CNDO/2 calculations (energy values in eV) *†

Atom	$\frac{1}{2}(I_s + A_s)$	$\frac{1}{2}(I_p + A_p)$	$\frac{1}{2}(I_d + A_d)$	β^0
C	14.051	5.572		21
N	19.316	7.275		25
S	17.650	6.989	0.713	18.150
H	7.176			9

* 1 eV = 1.602×10^{-19} J. † The quantities I , A , and β are defined in ref. 37.

distances and angles were taken from ref. 13 for the thioureas and from ref. 40 for the derivatives of thio-carbamic acids; they were kept constant for all the conformations studied.

For some of the ligands we carried out two types of calculation: (a) including $3d$ orbitals of the sulphur atom in the basis set; and (b) not including such orbitals. The main results for tmtu have already been presented²⁸; results for dmtu are shown in Figure 1

Table 3). From Figure 1 and Table 2, it is evident that two conformations are on the other hand accessible

TABLE 2

Energy (kJ mol^{-1}) of conformations corresponding to relevant points of the energy profiles for dmtu: (a) d orbitals in the basis set; (b) d orbitals not included in the basis set

Conformation/ $^\circ$ (ψ_2, ψ_1)	(a)	Energy	(b)
(0, 0)	0.00		0.00
(90, 0)	91.84		75.77
(180, 0)	23.99		-4.90
(180, 90)	109.30		69.82
(180, 180)			ca. 2.720

TABLE 3

Energy (kJ mol^{-1}) of conformations corresponding to relevant points of the energy profiles for tmtu. All calculations do not include d orbitals in the basis set

Conformation/ $^\circ$ (ψ_2, ψ_1)	Energy
(0, 0)	0.00
(90, 0)	58.19
(0, 90)	67.48
(0, 180)	ca. 2.595
(90, 180)	52.16

for dmtu and they should both be present in equilibrium in solution. Substantial agreement between the two types of calculations, with and without d orbitals, is also apparent. The only important difference is in the energy position of the two accessible conformations of dmtu. This energy difference is however only a few kcal mol^{-1} and it should not be regarded as signi-

tion. Therefore isomer (V) should not exist in detectable amounts in equilibrium with forms (I), (II),

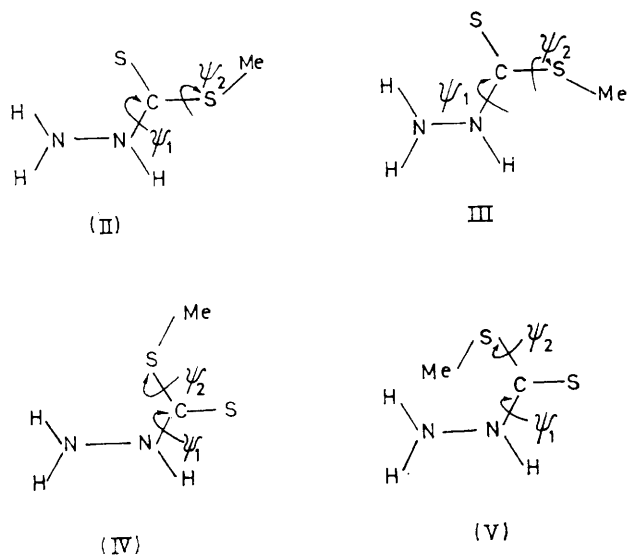


TABLE 4

Energy (kJ mol^{-1}) of conformations corresponding to relevant points of the energy profiles for dtca

Conformation/ $^{\circ}$ (ψ_1, ψ_2)	Energy
(0, 0)	0.00
(0, 180)	16.87
(180, 0)	ca. 126
(180, 180)	10.30

and (IV) because, precluding free rotation of the methyl group, it has a low probability of existence.

Moreover the energy barrier to rotation about the C-S bond (ψ_2) going from conformation (II) to (III) is one order of magnitude lower than that about the C-N bond (ψ_1). These results are in accord with n.m.r. spectra.⁴² By the latter technique only two forms are detectable at low temperature. One of the two resonances, however, is broader than the other and can be assigned to forms (II) and (III) in fast equilibrium because of the very low energy barrier to rotation. Theoretical studies on similar compounds, namely S-methyl esters of monothio- and of 2-methyldithiocarbamic acid, have also been completed. The calculations performed on these two molecules give energy profiles very similar to those exhibited by dtca, with one exception; conformation (III) of the ester of 2-methyldithiocarbamic acid is not accessible because of its high energy. The n.m.r. spectra of these compounds⁴² gave results in satisfactory agreement with these theoretical calculations.

In conclusion it seems that application of this semi-empirical quantum-mechanical procedure is useful for interpreting the experimental findings of systems of type (I). In particular the theoretical results for dmtu and tmtu compare well with corresponding

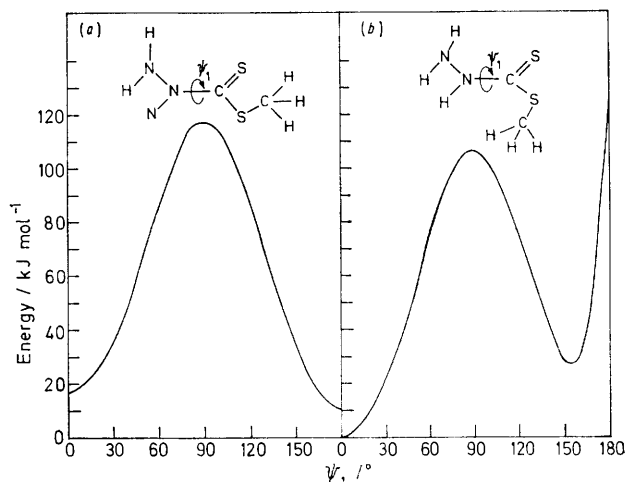


FIGURE 2 Energy profiles for dtca as a function of ψ_1 : (a) $\psi_2 = 180^{\circ}$; (b) $\psi_2 = 0^{\circ}$

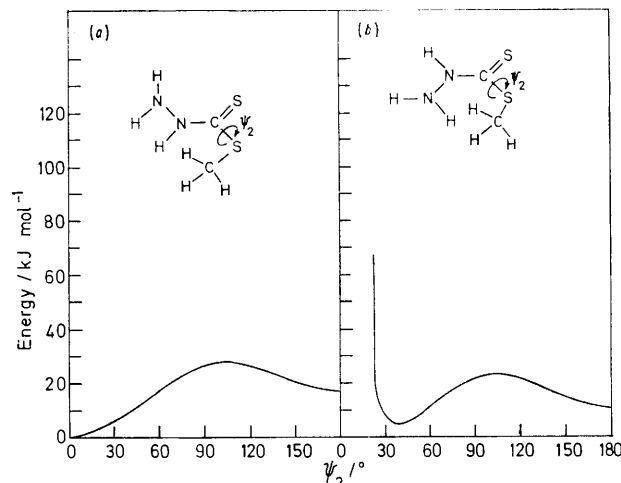


FIGURE 3 Energy profiles for dtca as a function of ψ_2 : (a) $\psi_1 = 0^{\circ}$; (b) $\psi_1 = 180^{\circ}$

n.m.r. spectra, whereas for the methyl ester of dtca, the application of more sophisticated methods and/or simultaneous consideration of several angles of rotation seems to be required.

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⁴² D. Gattegno and A. M. Giuliani, *Tetrahedron*, accepted for publication.