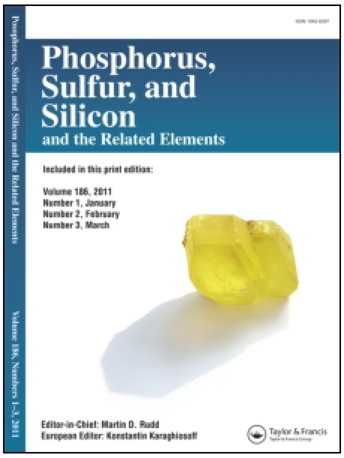


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

THE APPLICATION OF SIMPLE-HARMONIC-OSCILLATOR CALCULATIONS (HOSE-MODEL) TO CRYSTALLOGRAPHICALLY STUDIED *N*-PHOSPHORYL-*N,N'*-DISUBSTITUTED THIOUREAS

Janina Karolak-wojciechowska[a]
[a] Institute of General Chemistry, Technical University, Żwirki, Poland

To cite this Article Karolak-wojciechowska, Janina(1985) 'THE APPLICATION OF SIMPLE-HARMONIC-OSCILLATOR CALCULATIONS (HOSE-MODEL) TO CRYSTALLOGRAPHICALLY STUDIED *N*-PHOSPHORYL-*N,N'*-DISUBSTITUTED THIOUREAS', Phosphorus, Sulfur, and Silicon and the Related Elements, 25: 2, 229 — 235

To link to this Article: DOI: 10.1080/03086648508072738

URL: http://dx.doi.org/10.1080/03086648508072738

Phosphorus and Sulfur, 1985, Vol. 25, pp. 229–235
0308-664X/85/2502-0229/$15.00/0

THE APPLICATION OF SIMPLE-HARMONIC-OSCILLATOR CALCULATIONS (HOSE-MODEL) TO CRYSTALLOGRAPHICALLY STUDIED *N*-PHOSPHORYL-*N,N'*-DISUBSTITUTED THIOUREAS

JANINA KAROLAK-WOJCIECHOWSKA

Institute of General Chemistry, Technical University, 90-362 Łódź, Żwirki 36, Poland

(*Received September 12, 1984; in final form February 4, 1985*)

Simple-harmonic-oscillator calculation (HOSE-model) was applied to crystallographically studied molecules containing Y-shaped π-electron bonding unit. The method is tested for model compounds and then, applied to describe two different conformations of *N*-phosphoryl-*N,N'*-disubstituted thioureas. The contributions of resonance structures in the thiourea moiety are calculated. In molecules adopting an antiperiplanar conformation, the high contribution of polar structure creates more advantageous conditions for the formation of an intramolecular H-bond which stabilizes the molecule.

INTRODUCTION

The properties of *N*-phosphoryl-*N,N'*-disubstituted thiourea derivatives depend on the nature of substituents.[1] Structural investigations,[2,3,4,5] conducted parallel to chemical studies,[1,6,7] indicate the existence of a close relation between the properties of these compounds and their conformation.

The structures of five *N*-phosphoryl-*N,N'*-disubstituted thioureas[2,3,4,5] have been solved by x-ray analysis. The most important data describing their conformation and bond lengths in thiourea moiety are collected in Table I. The numbering system of the atoms and chemical formulas of the compounds **1**, **2**, **3**, **4** and **5** are given below.

The structures of *N,N'*-dibenzyl derivatives (**1**, **2** and **3**) were found to contain an intramolecular hydrogen bond N—H ··· O=P and antiperiplanar arrangement of the thiourea moiety. The absence of such H-bond in *N,N'*-dicyclohexyl derivatives (**4**, **5**) produces a change of the conformation to anticlinal. Differences in conformations are illustrated by the values of the torsion angle P—N(1)—C(1)—S as well as of the non-bonding contact P ··· S collected in Table I.

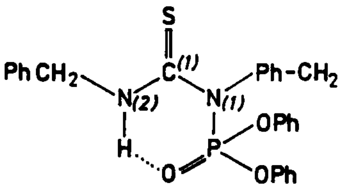
The thiourea skeleton in compounds under discussion fulfills the role of a π-electron fragment (molecule in molecule).[8] The thiourea molecule represents a 6-electron, 4-centre bonding unit[9] with sp^2 hybridized C(1) atom which forms three coplanar σ-bonds. The term Y-delocalization, for this type of compound, has been proposed by Gund.[10] This term is very convenient for Y-shaped compounds like urea or thiourea.

TABLE I

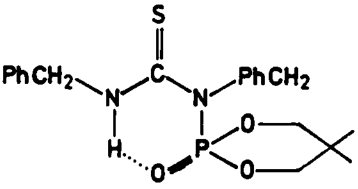
Comparison of some structural parameters of *N*-phosphoryl-*N*, *N'*-disubstituted-thioureas

compound	C(1)=S (Å)	N(2)—C(1) (Å)	N(1)—C(1) (Å)	N(1)—C(1)—N(2) (°)	torsion angle P—N(1)—C(1)—S (°)	P · · · S Å	type of H-bond	*R*-factor	ref.
1	1.666(2)	1.328(3)	1.413(3)	116.1(2)	169.2	4.278	intra	0.033	2
2	1.669(3)	1.325(4)	1.421(4)	115.3(3)	162.3	4.242	intra	0.0385	3
3	1.690(4)	1.320(6)	1.412(5)	116.9(4)	159.0	4.162	intra	0.051	4
4	1.651(4)	1.339(5)	1.415(5)	113.2(3)	125.7	4.028	no bond	0.069	5
5	1.648(10)	1.327(16)	1.459(15)	110.3(8)	91	3.73	inter	0.113	3[x]

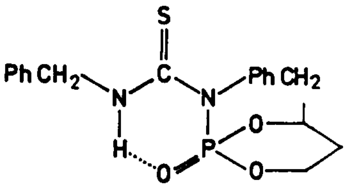
[x] This structure will not be used in the discussion.



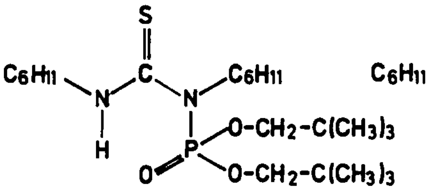
1



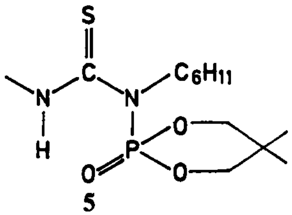
2



3

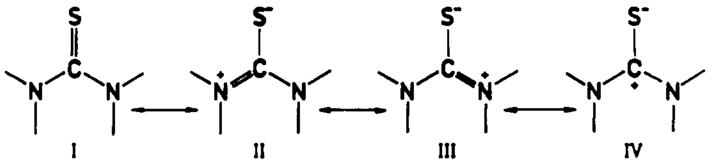


4



5

The four resonance structures (I, II, III and IV) are necessary for description of the thiourea molecule.



This paper presents the results of calculation of the contribution for these four resonance structures in the molecules of *N*-phosphoryl-*N*,*N*′-disubstituted thiourea derivatives. It has to be pointed out that the base for these calculations are bond lengths taken from crystallographic studies.[2,3,4,5] The use of x-ray measurement data in the more detailed description of the structurally investigated compounds, as it will be presented in this study, should be of wider interest. The application of the simple-harmonic-oscillator calculation proposed by Krygowski and co-workers[11,12] (HOSE-model) makes it possible.

EXPERIMENTAL

Description of the model. The model is characterized with very simple calculations. The experimental data, necessary to apply in the HOSE-model are the bond lengths from crystallographic studies of π-electron molecule (or π-electron fragment in the larger molecule). The investigated π-electron bonding unit is described by respective resonance structures. The stabilization energy E_{HOSE_i}, needed to transform the i-th resonance structure to the real molecule, is calculated in the HOSE-model, by applying the simple harmonic oscillator model (eq. 1)

$$E_{\mathrm{HOSE}_i} = \frac{1}{2}\left[\sum_{r=1}^{n_1}\left(R'_r - R_s^0\right)^2 k'_r + \sum_{r=1}^{n_2}\left(R''_r - R_d^0\right) k''_r\right] \tag{1}$$

where: R'_r and R''_r are the experimental bond lengths from the crystallographic studies; k'_r and k''_r—the corresponding to R'_r and R''_r force constants; n_1 and n_2 are the numbers of single and double bonds (respectively) in the i-th resonance structure; R_s^0 and R_d^0 are the standard single and double bonds respectively.

The force constant k_r, where both atoms of the bond are second-period atoms, is calculated by the empirical linear equation[11,12] (2)

$$k_r = a + bR_r \tag{2}$$

where **a** and **b** are found for each type of bond. In the present study, equation (2) does not hold in the case of the C—S bond according to the Badger formula.[13] The linear dependence of the force constant for C—S bond in the log/log system (eq. 3) has been determined on the basis of the literature data.[14,15,16,17]

$$\log k_r = 2.15 - 6.60 \log R_r \tag{3}$$

In practice, the calculation of the stabilization energy of the i-th resonance structure E_{HOSE_i} is done in the following way[11,12] (eq. 4)

$$E_{\mathrm{HOSE}_i} = 301.15\left[\sum_{r=1}^{n_1}\left(R'_r - R_s^0\right)^2 k'_r + \sum_{r=1}^{n_2}\left(R''_r - R_d^0\right)^2 k''_r\right] \tag{4}$$

where 301.15 is a multiplier which makes possibility to obtain E_{HOSE_i} in kJ · mol^{-1} taking bond lengths in Å. The total stabilization energy of a molecule is calculated from eq. (5)

$$E_{\mathrm{HOSE}} = \sum_i C_i E_{\mathrm{HOSE}_i} \tag{5}$$

where C_i is the contribution of the i-th resonance structure. The C_i is inversely proportional to its stabilization energy E_{HOSE_i} (eq. 6).

$$C_i = \left(E_{\mathrm{HOSE}_i}\right)^{-1} \Big/ \Sigma\left(E_{\mathrm{HOSE}_i}\right)^{-1} \tag{6}$$

The estimation of the standard deviations of E_{HOSE}; and C_i suggest the authors of the HOSE-model. In this paper, these e.s.d.'s are proposed to be calculated from the following formulas:

$$\sigma\left(E_{\mathrm{HOSE}_i}\right) = \left[\sum_{r=1}^{n}\left(\frac{d}{dR_r}E_{\mathrm{HOSE}_i}\right)^2 \sigma^2(r)\right]^{1/2} \tag{7}$$

$$\sigma(C_i) = \left[\left(\frac{d}{dE_{\mathrm{HOSE}_i}}C_i\right)^2 \sigma^2\left(E_{\mathrm{HOSE}_i}\right)\right]^{1/2} \tag{8}$$

where $\sigma(E_{\mathrm{HOSE}_i})$ is the e.s.d. of the value of E_{HOSE_i}; $\sigma(r)$ is e.s.d. for the R_r bond; n is the number of bonds in i-th resonance structure.

The method of calculations. The values of E_{HOSE_i} and C_i collected in Tables III and IV were calculated on the base of the formulas (4) and (6) taking into consideration relations (2) and (3). The standard data (R_d^0, R_s^0, a and b) are given in Table II.

TABLE II

The constants used in the HOSE model

Bond	R_s^0(Å)	R_d^0(Å)	a($\times 10^4$ Pa)	b($\times 10^4$ Pa)	Ref.
CN	1.458	1.274	43.18	−25.73	11.18
CO	1.428	1.209	52.35	−32.88	11
CS	1.820	1.610	—	—	19.20

TABLE III

E_{HOSE}-values (kJ · mol^{-1}) and resonance structure contribution C_i(%) in thiourea and urea molecules with e.s.d.'s in parenthesis

	thiourea			urea		
	E_{HOSE_i}	C_i	E_{HOSE}	E_{HOSE_i}	C_i	E_{HOSE}
I	93(1)	20.3(2)		85(4)	36.5(5)	
II	63(1)	29.8(3)	76(1)	139(4)	22.4(5)	124(3)
III	63(1)	29.8(3)		139(4)	22.4(5)	
IV	94(1)	20.1(2)		166(5)	18.7(5)	

TABLE IV

HOSE values (kJ · mol^{-1}) and resonance structures contribution C_i(%) for *N*-phosphoryl-*N*,*N'*-disubstituted thioureas

	resonance structure contribution				
compound	I	II	III	IV	E_{HOSE}
thiourea	20.3(2)	29.8(3)	29.8(3)	20.1(2)	76(1)
1	31(1)	36(1)	14(1)	19(1)	66(2)
2	30(1)	38(1)	13(1)	19(1)	65(2)
3	23(2)	45(2)	13(1)	19(1)	59(3)
4	39(2)	38(1)	13(1)	19(1)	62(2.5)

The literature structural data for urea[21] and thiourea[22] were used for the preparation of Table III. Table IV is based on our previously published results of *N*-phosphoryl-*N*,*N'*-disubstituted thioureas crystallographically studied.[2,3,4,5] These data, necessary in calculation, are collected, together with their e.s.d.'s, in Table I.

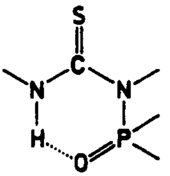
The calculation in terms of the HOSE-model can be performed only for those structures for which the e.s.d.'s of the bond lengths are $\leqslant$ 0.006 Å. Such value ensures that the calculation of the percentage contributions C_i, of the resonance structure will be $\sigma(C_i) \leqslant 2\%$. It is seen, that the data describing structure **5** (Table I) cannot be taken into consideration in discussion given below.

RESULTS

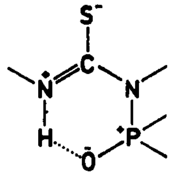
Model compounds. Krygowski and co-workers were applying, shortly given above, the HOSE-model to the description of the effect of substituents in the benzene rings geometry.[9,12,23,24] In the present study the HOSE-model is applied to acyclic systems with Y-shaped π-electron bonding unit (thiourea moiety) and therefore it must be tested. According to this, the calculations for model structures must be performed. In this case the molecules of urea and thiourea were used as model compounds. Both are Y-shaped π-electron molecules (6-electron, 4-center bonding unit) and can be described by the four resonance structures (I, II, III and IV) given in the introduction.

The contributions of four resonance structures (I, II, III and IV) in the molecules of urea and thiourea were calculated using the crystallographically found bond lengths. These values are taken from the literature and are equal for urea:[21] C=O of 1.262(2) and C—N = 1.338(4); and for thiourea:[22] C=S of 1.714(1) and C—N = 1.335(1) Å.

The results of calculation, together with e.s.d.'s, are collected in Table III. In the appropriate columns of this table the E_{HOSE_i} values for the four resonance structures as well as their percentage contributions C_i are given. The magnitude of the contribution of the non-polar structure I is of the greatest significance among the values in Table III. The considerably higher contribution of that form in urea (36.5(5)%) corresponds with the lower polarity of the carbonyl group C=O in that compound in comparison with the thiocarbonyl group C=S in thiourea (20.3(2)%). It is in good agreement with the described and explained[25] difference in the polarities of those two groups (C=O and C=S) which determine the properties of the model compounds.



5



6

The results obtained for model compounds provide a good base for the use of the HOSE-model to other compounds with the thiourea moiety which plays a role of "molecule in molecule".

N-phosphoryl-N,N'-disubstituted thioureas. All subsequent considerations will be performed for *N*-phosphoryl-*N*,*N'*-disubstituted thioureas with known solid state structures[2,3,4,5] and two types of conformations connected with different properties, as it was described in introduction. The calculated contributions of the resonance structure (I, II, III and IV) of thiourea moiety in compounds **1**, **2**, **3** and **4** together with the corresponding values for thiourea (taken from Table III for comparison) are presented in Table IV. It follows from those data, that the contribution of the resonance structure IV is identical for all cases under consideration, including thiourea, and is equal 19(1)%. Thus, only first three resonance structures (I, II and III) are important in the description of these molecules. It must be noted that only three important standard Lewis structures are considered by Harcourt[8] for Y-shaped 6-electron, 4-centred bonding unit.

The contributions of the structure III in *N*-phosphoryl thiourea derivatives (**1**, **2**, **3**, **4**) are also identical (av. 13(1)%), but they are considerably smaller than those calculated for unsubstituted thiourea molecule of 29.8(2)%. Such a large decrease of the contribution of the structure III (in structures **1**, **2**, **3** and **4** in comparison with thiourea) is due to the presence of a strong electronegative phosphoryl substituent. However, the equal contributions of this resonance structure indicate that variously substituted phosphoryl groups have similar electronegativity.

The effect of different conformation in the discussed molecules is manifested in the contributions of two resonance structures I and II (Table IV). The contribution of the polar form II of 28(1)% in the molecule with anticlinal conformation (cyclohexyl derivative) and, an average, 39(1)% in antiperiplanar form (benzyl derivatives) is determining the concentration of the formal positive charge on the atom N(2) of thiourea moiety. The larger contribution of that structure creates more advantageous conditions for the formation of an intramolecular hydrogen bond of the type N—H · · · O=P based on conjugated bond system. The sterically favored six-membered chelate ring is nearly planar (with experimental error of crystallographic data).[2,3,4] The phosphorus atom, according to Lewis octet structure, carries a formal positive charge.[26] So, two important resonance structures should be contributed in the discussed chelate ring. The polar ring **6** represents a polymethine-like state[27,28] and the larger contribution of this structure gives possibility of the strong H-bond formation.[29] This bond is observed in thioureas derivatives (**2**, **3** and **4**) having antiperiplanar conformation according to higher contribution of the polar resonance structure II. It is necessary to remind, that the electronegativity of *N*-phosphoryl substituents is similar. In the case of antiperiplanar conformation, the intramolecular H-bond stabilizes the molecule, making N → S rearrangement of the phosphoryl substituent impossible. On the other hand, the predominant contribution of the non-polar structure I in anticlinal conformation favours rotation around the C—N(1) long bond, and manifests itself in the easy N → S migrations of the phosphoryl substituent.[1]

The changes in the contribution of the nonpolar resonance structure I are reflected in the geometry of the Y-shaped skeleton. The increase in the contribution of that form in compound **4** is accompanied by a decrease of the valence angle N(1)—C(1)—N(2) (Table I) to 113.2(3)°. For compounds **1**, **2**, **3** (antiperiplanar conformation) this angle is, on average, 117.3(2)°. The direction of changes in that angle is in agreement with the Walsh rule.[30]

CONCLUSION

In the present paper the HOSE-model was applied to Y-shaped π-electron molecules (6-electron, 4-center bonding unit). The calculations were performed for *N*-phosphoryl-*N*,*N'*-disubstituted thiourea derivatives. The results show that the contribution of the positively charged nitrogen atom (with H-atom) depends on the conformation of the thiourea moiety. The large contributions of that polar form in the molecules with antiperiplanar conformation give better conditions for forming of the intramolecular H-bond. The chelate ring formation represents a polymethine-like state. The polar limit structure of this ring is favoured. The absence of intramolecular H-bond in the molecule causes the anticlinal conformation of the thiourea moiety (with easy N → S rearrangement).

An extension of similar applications of the HOSE-model can give the possibility for the better application of the crystallographic data for other structures containing π-electron fragment (molecule in molecule). The estimation of the stabilization energy (E_{HOSE}) for bicyclic 2-thiohydantoin derivatives (crystallographically studied) showing different chemical reactivity,[31] can be further exemplification of usefulness of this approach.

ACKNOWLEDGMENT

The author would like to express her gratitude to Professors M. Mikołajczyk and T. M. Krygowski for the valuable comments and suggestions made, while this paper was being prepared.

References

1. M. Mikołajczyk, P. Kiełbasiński and W. Basiński, *J. Org. Chem.*, **49**, 899 (1984).
2. J. Karolak-Wojciechowska, M. W. Wieczorek, M. Mikołajczyk, P. Kiełbasiński, Y. T. Struchkov and M. Y. Antipin, *Acta Cryst.*, **B-35**, 877 (1979).
3. J. Karolak-Wojciechowska, M. W. Wieczorek, Y. T. Struchkov, M. Y. Antipin, M. Mikołajczyk, P. Kiełbasiński and A. Sut, *Phosphorus and Sulfur*, **17**, 141 (1983).
4. J. Karolak-Wojciechowska, M. W. Wieczorek, M. Mikołajczyk, A. Sut, P. Kiełbasiński, Y. T. Struchkov and M. Y. Antipin, *Acta Cryst.*, **C-39**, 587 (1983).
5. J. Karolak-Wojciechowska, M. Mikołajczyk, P. Kiełbasiński, and A. Sut, *Phosphorus and Sulfur*, **21**, 221 (1984).
6. M. Mikołajczyk, P. Kiełbasiński and Z. Goszczyńska, *J. Org. Chem.*, **42**, 3629 (1977).
7. M. Mikołajczyk and P. Kiełbasiński, *Tetrahedron*, **37**, 233 (1981).
8. R. Daudel, R. Lefebvre and C. Moser, "Quantum Chemistry Method and Applications." Interscience Publishers Inc., New York (1959).
9. R. D. Harcourt, Qualitative Valence-Bond Descriptions of Electron-Rich Molecules: Pauling "3-Electron Bonds" and "Increased-Valence" Theory. Lect. Notes Chem. **30**, (1982).
10. P. Gund, *J. Chem. Educ.*, **49**, 100 (1972).
11. T. M. Krygowski, R. Anulewicz and J. Kruszewski, *Acta Cryst.*, **B-39**, 732 (1983).
12. T. M. Krygowski and T. Więckowski; *Croat. Chim. Acta*, **54**, 193 (1981).
13. S. Walker and H. Traw, Spectroscopy Vol. 2 Champman and Hall LTD and Science (1970).
14. G. Herzberg, "Infra-Red and Raman Spectra," New York (1945).
15. D. C. Monle and C. R. Subramanian, *Can. J. Chem.* **47**, 1011 (1969).
16. Topics in Sulfur Chem. Vol. 4, Ed. by E. Senning. Georg Thieme Publishers, Stuttgart (1979) p. 192.
17. T. L. Cottrell, The Strengths of Chemical Bonds, London (1954).
18. R. D. Gilardi and J. L. Karle; *Acta Cryst.*, **B-28**, 1635 (1972).
19. H. W. Kroto and B. M. Landsburg; *J. Spectrosc.*, **62**, 376 (1976).
20. L. Pierce, M. Kayski; *J. Chem. Physics*, **35**, 479 (1961).
21. D. Mullen; *Acta Cryst.*, **B-36**, 1610 (1980).
22. A. Kutoglu, Ch. Scheringer, H. Meyer and A. Schweig, *Acta Cryst.*, **B-38**, 2626 (1983).
23. T. M. Krygowski, *J. Chem. Research (S)*, 238 (1984).
24. T. M. Krygowski, R. Anulewicz; *Materials Science*, **10**, 145 (1984).
25. "Organic Chemistry of Sulfur," Ed. by S. Oae, Plenum Press, New York, London (1977) p. 189.
26. E. Cartmell and G. G. A. Fowles. "Valency and Molecular Structures." Butterworths (1977).
27. S. Dähne and S. Kulpe, "Structural Principles of Unsaturated Organic Compounds." Abh. Akad. Wiss. DDR, **8**, Berlin; Academic-Verlag (1977).
28. S. Kulpe and S. Dähne, *Acta Cryst.* **B-34**, 3616 (1978).
29. K. Szulzewsky, B. Schulz, A. Kulpe and J. Kreutzmann, *Acta Cryst.*, **C-40**, 280 (1984).
30. A. D. Walsh, Discuss, *Faraday Soc.*, **2**, 18 (1947).
31. J. Karolak-Wojciechowska, M. Mikołajczyk, A. Zatorski, K. Kieć-Kononowicz and A. Zejc, *Tetrahedron*, in press.