binding. To obtain this minimum in the energy in a model calculation, it would now be sufficient to consider only nearest-neighbour interactions.

As to physical properties, the incommensurate modulation appears not to have a strong effect on the electrical conductivity. As mentioned above, no anomaly has been observed around 200 K (Oostra, 1985), the temperature where the modulation sets in. The effects of the modulation are, however, noticeable in the magnetic susceptibility. Above about 10 K the compound behaves as a normal one-dimensional $S = \frac{1}{2}$ antiferromagnet with a spin-spin exchange constant of 7 K (Korving, Hijmans, Brom, Oostra, Sawatzky & Kommandeur, 1983). The expected maximum at 9 K in the magnetic susceptibility (Bonner & Fisher, 1964) is, however, entirely absent and the magnetic susceptibility rises steadily down to 1·65 K, where a phase transition occurs. The overall shape of the magnetic susceptibility curve resembles that of a spin glass. As noted by Hijmans (1985), this probably indicates a distribution of exchange constants along the TCNQ chains. This phenomenon can be understood when one takes into account the influence of the incommensurate periodic potential of the DMM ions on the TCNQ chains. The exchange constants along the TCNQ chains will follow this modulation and this is not a minor effect since exchange constants are quite sensitive to the magnitude of a periodic potential (Kramer & Brom, 1984).

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Application of the HOSE (Harmonic Oscillator Stabilization Energy) Model to Y-Shaped Molecules

BY JANINA KAROLAK-WOJCIECHOWSKA

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

Abstract

The HOSE model has been applied to molecules containing the Y-shaped π-electron fragment of the thiourea (or urea) molecule. The contributions of the resonance structures (c_i) for this fragment of the molecules and the value of the stabilization energy (E_{HOSE}) have been estimated from bond lengths determined by X-ray methods. On the basis of these values relationships between the structures and

properties of the compounds have been found. For pairs of isomeric compounds, the higher value of E_{HOSE} is observed for the more stable isomer. The contributions of resonance structures in compounds containing the thioamidine group depend strongly on the electronegativity of the substituents bonded to the N atoms. The same effect has been found in N-multisubstituted thiourea (and urea) derivatives. It was also observed that the c_i values of thiourea derivatives are dependent on the conformation of the thiourea skeleton.

Introduction

The HOSE model (Więckowski & Krygowski, 1981; Krygowski, Anulewicz & Kruszewski, 1983; Krygowski & Anulewicz, 1984; Krygowski, 1982) makes it possible to estimate the stabilization energy (E_{HOSE}) of π-electron arrangements. E_{HOSE} is the energy needed to transform the geometry of a particular resonance structure to the geometry of the real molecule. The percentage contribution (c_i) of the ith resonance form is inversely proportional to its stabilization energy E_{HOSE_i}. For the calculation of c_i only precisely determined bond lengths in the chosen π-electron fragment are needed. For example, to ensure c_i with an accuracy of $\pm 2\%$, $\sigma \leq 0.006$ Å are required. [For the method of $\sigma(c_i)$ calculation see Karolak-Wojciechowska (1985).]

The HOSE model was applied by its authors to search for structure correlations in aromatic compounds. The present application of the HOSE model involves two points: (i) The contribution of resonance structures is related to the properties of the group of compounds under discussion with one requirement: the properties must be due to the presence of a common π-electron fragment. This fragment plays the role of a 'molecule in a molecule' (Daudel, Lefebvre & Moser, 1959). (ii) The method can be used for any π-electron fragment whether cyclic or acyclic.

In the present paper, the HOSE-model methodology is applied to acyclic systems with Y-shaped π-electron bonding units (Y-delocalized systems). The term Y-delocalization was proposed by Gund (1972) for four-center-six-electron bonding units. Some examples of such atom arrangements are molecules (1) to (6). Included among them are the molecules of urea (1) and thiourea (2).
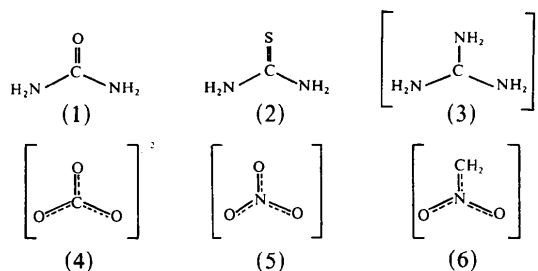
We shall concentrate the discussion on three groups of compounds containing Y-delocalized urea or thiourea fragments in the molecule. Before we do that, however, the relevant problems have to be discussed for model compounds. The applicability of the HOSE model to Y-shaped π-electron bonding units will be tested for two groups of model compounds: (i) simple urea and thiourea molecules, and (ii) a 2-thiohydantoin molecule, only a fragment of which has π-electron character.

The aim of this paper is to present a summary of all variants of a deeper interpretation of the structure results for Y-shaped molecules on the basis of HOSE-model application. Accordingly, it will be also necessary to mention details of some earlier papers.

Discussion of model compounds

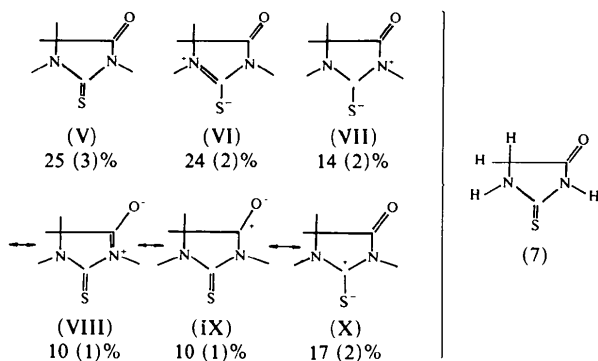### Comparison of urea and thiourea molecules

For the valence-bond description of molecules (1) and (2), four important resonance structures [(I)–(IV)] have been proposed. As the method of estimating the percentage contribution for these structures was described in an earlier publication (Karolak-Wojciechowska, 1985), we shall only give a short interpretation of the numerical results here. The contributions of resonance structures (I), (II), (III) and (IV) in the urea (1) and thiourea (2) molecules are given below following their formulas [for the structures of thiourea and urea see respectively: Kotoglu, Scheringer, Mayer & Schweig (1982) and Mullen (1980)]. The differences between the contributions of

	(I)	(II)	(III)	(IV)
(1)	36·5 (1·0)%	22·4 (5)%	22·4 (5)%	18·7 (5)%
(2)	20·3 (2)%	29·8 (3)%	29·8 (3)%	20·1 (2)%
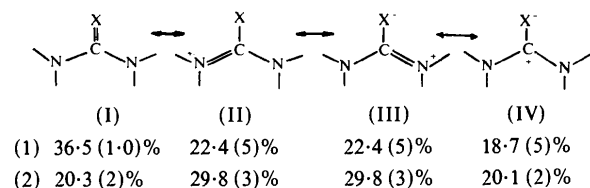
the various resonance structures are well correlated with the differences in properties of both compounds. The greater polarity of the thiourea molecule (Oae, 1977) in comparison with that of the urea molecule coincides with the greater total contribution of polar forms (II), (III) and (IV) in (2).

Model calculation of 2-thiohydantoin

From the point of view of valence-bond theory, 2-thiohydantoin (7) can be described in terms of six important resonance structures [(V)–(X)]. The percentage contributions of these structures, given below each resonance structure, were evaluated using the bond lengths reported by Walker, Folting & Merritt (1969). The values show a good correlation with the chemical properties of 2-thiohydantoin (Kharasch & Meyers, 1966). The high value for the contribution

(1) (2) (3) (4) (5) (6)

(V)
25 (3)%

(VI)
24 (2)%

(VII)
14 (2)%

(7)

(VIII)
10 (1)%

(IX)
10 (1)%

(X)
17 (2)%

Table 1. *Contributions of resonance structures* (%) *and stabilization energy* E_{HOSE} (kJ mol^{-1}) *in aryl-aminothiazines and -thiazolidines* (12)

| Q | Contribution of structures | | | | |
	c_I	c_{II}	c_{III}	c_{IV}	E_{HOSE}
H[a]	12(0·5)	17(1)	56(2)	15(1)	74(5)
CH$_3$[b]	12(0·5)	16(1)	58(3)	14(1)	68(6)
COAr[c]	6(0·5)	6(0·5)	80(3)	8(1)	45(1)
SO$_2$CH$_2$[d]	5(0·5)	5(0·5)	84(3)	6(0·5)	29(3)

References: (a) Petrovic, Ribar, Argay, Kálmán & Nowacki (1977), Kálmán, Argay, Ribar & Toldy (1977), Argay, Kálmán, Kapor & Ribar (1977); (b) Argay, Kálmán, Kapor & Ribar (1980); (c) Argay, Kálmán, Nahlovski & Ribar (1975); (d) Kálmán & Argay (1978a,b).

of non-polar form (V) is indicative of the considerable stability of the molecule. The total contribution of structures with polar thiocarbonyl groups [(VI), (VII) and (X)] is much larger than that of structures with polar carbonyl groups [(VIII), (IX)]. This confirms the observed higher polarity of the thiocarbonyl group and the ease of *S*-substitution in 2-thiohydantoin (Oae, 1977). The experimentally determined chemical non-equivalence of N atoms in this molecule (Elmore, 1958) is confirmed by the different percentage contributions of structures with a formal positive charge on their N atoms (VI and VII).

Application to Y-shaped molecules

The discussion of model compounds presented above makes it possible to apply the HOSE model to the description of some properties of compounds containing Y-delocalized urea and thiourea skeletons. What follows will be based on three groups of compounds which allow three different examples of the use of X-ray results to be presented.

Reactivity and delocalization of π electrons

Our objective (Karolak-Wojciechowska, Mikołajczyk, Zatorski, Kieć-Kononowicz & Zejc, 1985) was to discuss the relationship between the chemical stability of isomeric compounds (8) to (11) and the delocalization of π electrons. The formulas of these pairs of isomers are given below, together with the values of E_{HOSE} calculated on the basis of structure results (Kieć-Kononowicz, Zejc, Mikołajczyk, Zatorski, Karolak-Wojciechowska & Wieczorek, 1980, 1981; Karolak-Wojciechowska *et al.*, 1985). The pair of compounds (9) and (11) is chemically more stable (Kieć-Kononowicz & Karolak-Wojciechowska,

1987); this is connected with significantly higher values of the stabilization energy E_{HOSE} of the π-electron arrangements for these two compounds than for compounds (8) and (10).

Stabilization energy and electronegativity of substituents

Another example of the application of the HOSE model to compounds with Y-shaped π-electron fragments is the analysis of the effect of substituents with variable electronegativity on the contribution of resonance structures in arylaminothiazines and -thiazolidines described by formula (12). Structural investigations of a series of such compounds have been carried out by Kálmán *et al.* (see footnotes of Table 1). The thioamidine group present in these compounds plays an important role in a number of biologically active compounds. It is, thus, of considerable importance to be able to predict changes in the properties of these compounds brought about by differences in substituent electronegativity. Since the thioamidine group can be derived from the thiourea skeleton, the resonance structures (I), (II), (III) and (IV) can be used for its valence-bond description. Hence, crystallographically determined bond lengths in compounds (12) have been used to estimate the contributions of these four resonance structures.
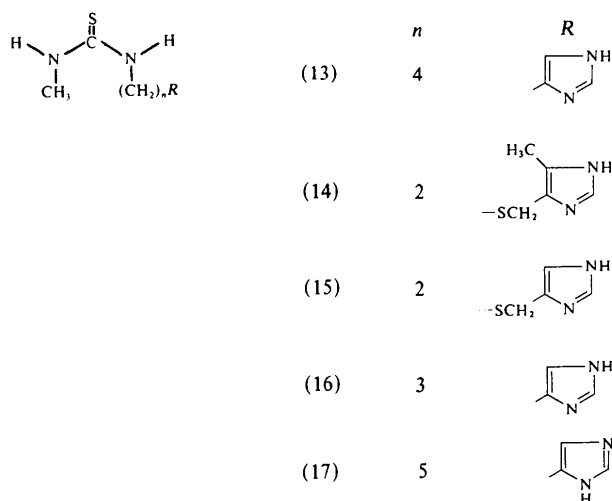

Q

H

CH$_3$

COAr

SO$_2$CH$_2$

(12)
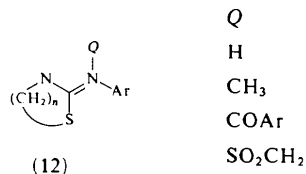
The calculations have been carried out for arylaminothiazines and -thiazolidines (12) where the variable elements are the Q and aryl substituents. The compounds chosen were divided into four groups differing in Q substituents. The mean values of estimated resonance-structure contributions for each group are given in Table 1. Let us analyse, as an example, the contribution of structure (III). For compounds where the substituents are an H atom or a methyl group the contributions of this structure are similar and amount to about 50%. For the unsub-

(8) $n = 2$, $E_{HOSE} = 46$ (10) kJ mol^{-1}
(10) $n = 3$, $E_{HOSE} = 36$ (2)

(9) $n = 2$, $E_{HOSE} = 85$ (4)
(11) $n = 3$, $E_{HOSE} = 88$ (4)

stituted thiourea molecule, the contribution of this structure is 30%. On replacing the substituent with a more electronegative one the contribution of structure (III) increases significantly to about 80%. At the same time, the total stabilization energy E_{HOSE} for compounds with a more electronegative substituent (SO_2CH_2) is much lower. Such an analysis could even provide a basis for determining the electronegativity of substituents.

Conformation of N-multisubstituted ureas and thioureas

Another example of the proposed approach is the relationship between the conformation of N-multi-substituted thioureas, on the one hand, and the values of the contributions of resonance structures, on the other. Among thiourea derivatives, two groups of compounds will be discussed here, namely N,N'-disubstituted [(13)-(17)] and N-phosphoryl-N,N'-

disubstituted [(18)-(22)] derivatives. The estimations of the contribution of resonance structures (I), (II), (III) and (IV), given in Table 2, have been based on the structure analysis results.
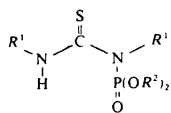
(18) $R^1 = PhCH_2$, $R^2 = Ph$
(19) $R^1 = PhCH_2$, $R^2 + R^2 = -CH(CH_3)(CH_2)_2-$
(20) $R^1 = PhCH_2$, $R^2 + R^2 = -CH_2C(CH_3)_2CH_2-$
(21) $R^1 = cyclohexyl$, $R^2 + R^2 = -CH_2C(CH_3)_2CH_2-$
(22) $R^1 = cyclohexyl$, $R^2 = -CH_2C(CH_3)_3$

Analysing the values collected in Table 2 one can see that the contribution of structure (IV) is identical in all cases under consideration, including thiourea, and amounts to about 19%. It is of wider interest that the contribution of (IV) is also similar in the S-thiophosphorylisothiourea derivative (23) (Blonski et al., 1982). Only three of the four structures pro-

Table 2. *Contributions of resonance structures c_i (%) in thiourea derivatives with e.s.d.'s in parentheses*

Compound	C=S(Å)	C-N(Å)	c_I	c_{II}	c_{III}	c_{IV}
(2)^a	1·714(1)	1·335(1) 1·335(1)	20·3(2)	29·8(3)	29·8(3)	20·1(2)
(13)^b	1·709(4)	1·336(5) 1·326(3)	20(1)	28(1)	32(2)	20(1)
(14)^c	1·711(2)	1·338(3) 1·325(3)	20(0·5)	27(1)	33(1)	20(0·5)
(15)^c	1·707(2)	1·337(2) 1·330(2)	21(0·5)	28(0·5)	31(0·5)	20(0·5)
(16)^d	1·699(5)	1·333(6) 1·317(6)	21(1)	26(2)	34(2)	19(1)
(17)^e	1·715(5)	1·330(6) 1·323(6)	19(1)	29(2)	32(2)	20(1)
(18)^f	1·666(2)	1·328(3) 1·413(3)	31(1)	36(1)	14(1)	19(1)
(19)^g	1·669(3)	1·325(4) 1·421(4)	30(1)	38(1)	13(1)	19(1)
(20)^h	1·690(4)	1·320(6) 1·412(5)	23(2)	45(2)	13(1)	19(1)
(21)^h	1·65(1)	1·33(2) 1·46(2)	36(6)	32(4)	12(2)	20(3)
(22)^i	1·651(4)	1·339(5) 1·415(5)	39(2)	28(1)	13(1)	19(1)
(23)^j	1·783(5)	1·319(6) 1·297(7)	15(1)	28(2)	40(3)	17(1)

References: (a) Kotoglu *et al.* (1982); (b) Kamenar, Prout & Ganellin (1973); (c) Glover & Prout (1981a); (d) Glover & Prout (1981b); (e) Prout, Critchley, Ganellin & Mitchell (1977); (f) Karolak-Wojciechowska, Wieczorek, Mikołajczyk, Kiełbasiński, Struchkov & Antipin (1975); (g) Karolak-Wojciechowska, Wieczorek, Mikołajczyk *et al.* (1983); (h) Karolak-Wojciechowska, Wieczorek, Struchkov *et al.* (1983); (i) Karolak-Wojciechowska, Mikołajczyk, Kiełbasiński & Sut (1984); (j) Blonski *et al.* (1982).

posed for this π-electron system play a significant role in differentiating the properties of thiourea and its derivatives.
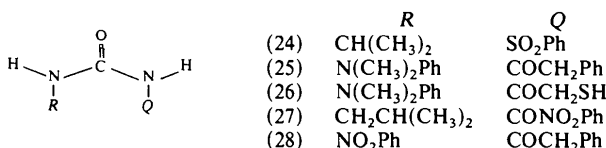
(23)
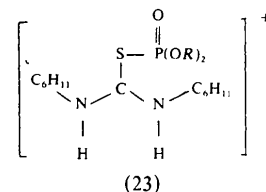
A series of four N,N'-disubstituted thiourea structures [(13)-(17)] with analogous conformations are listed in Table 2. The contributions of the various resonance structures for these compounds are, within error, identical to the values calculated for unsubstituted thiourea. These identical contributions are due to the similar electronegativity of both substituents in the thiourea skeleton (electronegativity similar to an H atom). The values of contributions may be changed by changing the character of the substituent, as shown by the values for N-phosphoryl-N,N'-disubstituted derivatives [Table 2, compounds (18) to (22)]. The presence of a strongly electronegative phosphoryl group considerably reduces the contribution of the polar form (III), whose phosphoryl substituent is at an N atom with a formal positive charge. A similar tendency is also observed for urea derivatives with electronegative substituents, as is illustrated by the values in Table 3 for compounds (24) to (28). Owing to the presence of strong inter- and intramolecular H bonds in all

Table 3. *Contributions of resonance structures (%) in urea derivatives with e.s.d.'s in parentheses*

Compound	C=O (Å)	C–N (Å)	c_I	c_{II}	c_{III}	c_{IV}
(1)[a]	1·262(2)	1·338(4) 1·338(4)	37(1)	22(0·5)	22(0·5)	19(0·5)
(24)[b]	1·239(4)	1·325(4) 1·396(4)	49(2)	21(1)	14(0·5)	16(1)
(25)[c]	1·227(2)	1·333(2) 1·406(2)	67(1)	17(0·5)	12(0·5)	14(0·5)
(26)[d]	1·224(3)	1·338(3) 1·399(3)	59(1)	16(0·5)	12(0·5)	13(0·5)
(27)[e]	1·230(5)	1·328(5) 1·413(5)	55(2)	19(1)	12(0·5)	14(0·5)
(28)[e]	1·240(4)	1·328(4) 1·392(4)	49(2)	21(4)	14(0·5)	16(1)

References: (a) Mullen (1980); (b) Dupont, Didberg & Vermeire (1979); (c) Ohashi, Uchida, Sasada, Kinoshita & Endo (1984); (d) Uchida, Ohashi, Sasada, Koneko & Endo (1984a); (e) Uchida, Ohashi, Sasada, Koneko & Endo (1984b).

these structures, the differences in the contributions among similar molecules are much greater than in the case of thiourea derivatives. This is because in the latter case the H bonds are much weaker.

	R	Q
(24)	$CH(CH_3)_2$	SO_2Ph
(25)	$N(CH_3)_2Ph$	$COCH_2Ph$
(26)	$N(CH_3)_2Ph$	$COCH_2SH$
(27)	$CH_2CH(CH_3)_2$	$CONO_2Ph$
(28)	NO_2Ph	$COCH_2Ph$

Returning now to the data collected in Table 3, one can see differences in the contributions of the first two resonance structures for compounds with phosphoryl groups [(18) to (22)]. These compounds (Karolak-Wojciechowska *et al.*, 1985) differ in the conformation of the thiourea skeleton. For the N,N'-dibenzyl derivatives (18), (19) and (20) the conformation is antiperiplanar, while for the N,N'-dicyclohexyl derivatives (21) and (22) it is anticlinar. Structural investigations of compounds with antiperiplanar conformations have shown the presence of intramolecular N–H···O=P hydrogen bonds. The differences between the two types of compounds are reflected in the contributions of resonance structures (I) and (II) (Table 2).

Concluding remarks

In some cases the application of the HOSE model offers a simple mode for correlating the bond lengths in Y-shaped π-electron fragments with the percentage contributions of their resonance structures. This is important from the viewpoint of some properties characterizing the group of structurally investigated compounds.

It seems that the approach presented here may also be applied to other π-electron systems. Thiourea derivatives are only one example of the possibilities for deeper interpretation of structural results. Using literature data, the results of structural investigations can provide further chemical insight.

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SHORT COMMUNICATIONS

Contributions intended for publication under this heading should be expressly so marked; they should not exceed about 1000 words; they should be forwarded in the usual way to the appropriate Co-editor; they will be published as speedily as possible.

On the dualistic interpretation of the symmetry of the incommensurately modulated structure of

NbTe$_4$. By SANDER VAN SMAALEN, *Laboratory of Inorganic Chemistry, Materials Science Centre, University of Groningen, Nijenborgh 16, 9747 AG Groningen, The Netherlands*

Abstract

The dualistic interpretation of the symmetry of the incommensurately modulated structure of NbTe$_4$ is considered. It is shown that the previously determined structure is in full accordance with this description of the symmetry.

The symmetry of incommensurately modulated structures can be described by the so-called superspace groups (de Wolff, Janssen & Janner, 1981). Then, for each independent modulation wave vector an additional coordinate is defined, and the symmetry operations are given by $3 - d$ reducible matrices operating in a $(3 + d)$-dimensional space.

De Wolff (1984) has developed an alternative description in which the symmetry of the basic structure and the modulation are given by separate three-dimensional space groups. It was shown that for one-dimensional modulations this dualistic description and the superspace-group approach are equivalent, whereas for higher-dimensional modulations, the dualistic description is the less general one (de Wolff, 1984).

Recently, Prodan & Boswell (1987) have applied the dualistic interpretation of the symmetry to the incommensurately modulated phase of NbTe$_4$. One of their conclusions was that the structure of NbTe$_4$ as determined from X-ray diffraction by van Smaalen, Bronsema & Mahy (1986)* is not in accordance with the dualistic description of the symmetry. This would mean that the symmetry restrictions derived for the modulation functions are already in error. In this note it will be shown that the previously determined structure exhibits the full dualistic symmetry.

From X-ray diffraction the $(3 + 1)$-dimensional super-space group was determined as $W^{P4/mcc}_{1\,\bar{1}\bar{1}1}$ with modulation wave vector $\mathbf{q} = (\frac{1}{2}, \frac{1}{2}, 0\cdot691)$ (van Smaalen *et al.*, 1986). In the dualistic approach, two 3D space groups have to be specified, one for the basic structure and one for the modulation wave. For NbTe$_4$ they are $G_B = P4/mcc$ and $G_M = I4/mmm$, respectively (Prodan & Boswell, 1987).

In Fig. 1 a projection of the basic structure on the *ab* plane is given. As defined by van Smaalen *et al.* (1986), we will use the larger unit cell $A \times B \times C$ ($C = c$), in which the modulation wave vector has only one irrational component: $\mathbf{q}_i = (0, 0, 0\cdot691)$. In order to explain the different symmetry operators, the two atoms denoted by 1 and 2 will be considered in more detail.

In the basic structure these two atoms are related by a *c*-glide plane perpendicular to *A*. In the superspace group the symmetry operation between those two atoms is $(\frac{c}{1})$.
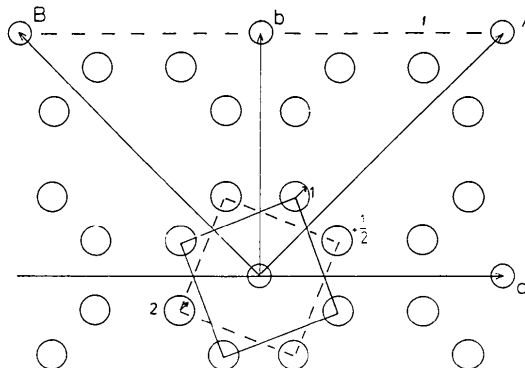

Fig. 1. Projection of the basic structure. Large circles denote Te atoms, small circles denote Nb atoms. Shown are the original (*a, b*) unit cell and the transformed (*A, B*) cell. The atoms indicated by 1 and 2 correspond to those in Fig. 2.

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* Fig. 4 of van Smaalen *et al.* (1986) contains some errors. B_{12} for Nb in Table 8 should be $-0\cdot03899$ (2), in accordance with the values given in Table 7.