A STUDY OF STRUCTURE OF *meta* AND *para* SUBSTITUTED PHENYL AND BENZOYL ISOTHIOCYANATES BY THE MNDO METHOD

Ivan DANIHEL[a], Pavol KRISTIAN[a], Stanislav BÖHM[b] and Josef KUTHAN[b]

[a] *Department of Organic Chemistry, Faculty of Natural Sciences,*
P. J. Šafárik University, 041 67 Košice and
[b] *Department of Organic Chemistry,*
Prague Institute of Chemical Technology, 166 28 Prague 6

On the basis of the optimized MNDO calculations of a selected series of *meta* and *para* substituted phenyl and benzoyl isothiocyanates it has been found that the —NCS group is non-linear in both the cases (the deviation from linearity is about 9°). For the phenyl isothiocyanates the values of CNC angles are in the region of 146·1°—149·0°, and for the benzoyl isothiocyanates the respective regions for the CNC and OCN angles are 146·4°—152·1° and 117·1°—118·5°. In the *meta* substituted benzoyl isothiocyanates the —CONCS group is perpendicular to the phenyl residue. The results are discussed from the point of view of the electron distribution and dipole moments of the compounds studied.

Relatively few experimental data are available about the structure of phenyl iso-thiocyanates, and practically no quantitative data can be found for acyl isothio-cyanates. Various structures suggested for the —NCS group on the basis of experiments follow from applications of experimental methods of quite different nature[1]. Hence, the data obtained by various physico-chemical methods do not always lead to the same conclusions about structure of these compounds. Differences appear in the predictions of energetically advantageous conformations, in estimation of the valence angles RNC or NCS. Ethyl isothiocyanate can be given as an example, its IR spectra[2] indicating two energetically favourable rotameric forms, probably the antiperiplanar and the synclinal arrangements of the methyl and —NCS groups, whereas a microwave spectral study[3] led to a conclusion in favour of the synperi-planar arrangement, and theoretical calculations denote the anticlinal conformation as the most stable one[4]. For isothiocyanic acid and alkyl isothiocyanates experimental results[2,3,5,6] concordantly state that the RNC (HNC) angle distinctly differs from 180°, the molecules possessing the C_s symmetry. Linear arrangement is considered for the —NCS group. An interesting discussion is published[7] for the silyl isothio-cyanate molecule where the conclusions deduced from the microwave spectra indicate linear arrangement of the whole Si—N=C=S chain (*i.e.* C_{3v} symmetry)[8]. More recent results lead to the same conclusion[9], *viz.* that the ground state of the H₃SiNCS

molecule can be described by the mesomeric forms $H_3Si\overset{(-)}{=}N\overset{(+)}{=}C=S$ and $H_3Si\overset{(+)}{-}N\equiv$

$\equiv\overset{(-)}{C}-S$. Similarly, for silylisocyanate[10,11] IR and microwave spectra also are consistent with the linear structure of the SiNCO fragment, but the electron diffraction data[12] indicate (in analogy with the *ab initio* calculations[13]) the SiNC angle about 150°. The electron diffraction data for trimethylsilyl isothiocyanate and isocyanate[14] also lead to the conclusion of non-linear arrangement of the SiNC chain, the respective angle reaching the value about 150°. With aryl isothiocyanates the situation is similarly ambiguous. So *e.g.* the IR and Raman spectra of phenyl isothiocyanate indicate the C_{2v} molecular symmetry[15], whereas other authors[16] suggest, from the IR spectra, the probable structure with C_1 symmetry. Still other authors[17] ascribe (from the Raman spectra of phenyl isothiocyanate) the C_s symmetry with the dihedral angle between the benzene ring plane and the —NCS group equal to 90° (Scheme 1). In these cases, too, the linear arrangement of the —NCS group
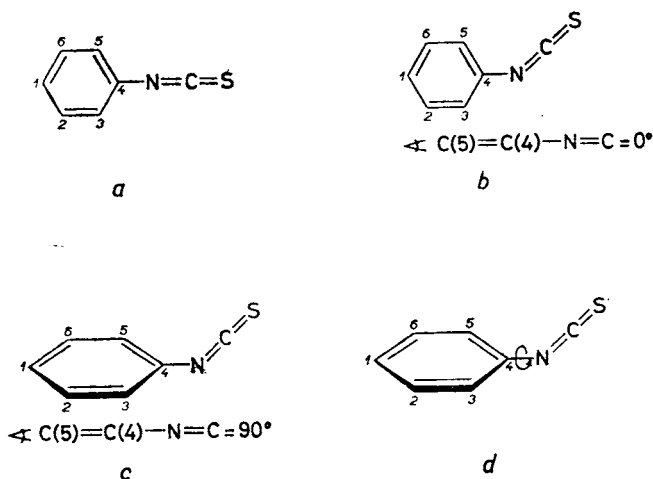

SCHEME 1

is considered. However, crystallographical data for *para* bromophenyl isothiocyanate indicate non-linear arragement of the —NCS group[18]. But the view about non-linearity of the —NCS group appeared earlier, *viz.* on the basis of the *ab initio* calculations of structural parameters of isothiocyanic acid[19]. As there are semi-empirical quantum chemical methods which can predict realistic molecular structures, we considered it useful in the present work to deal with structural problems of *meta* and *para* substituted phenyl and benzoyl isothiocyanates and to create their models on the basis of the MNDO calculations. The MNDO calculations are discussed along with some previous experimental results[20,21] and results of measure-
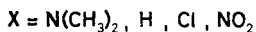
ments of dipole moments of *meta* and *para* substituted benzoyl isothiocyanates. With respect to the selected series of compounds we also investigated the effect of substituents on the structure of the derivatives studied.

$X = N(CH_3)_2$, H , Cl , NO_2
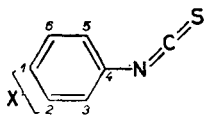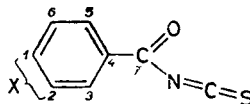
CALCULATIONS AND EXPERIMENTAL

The calculations of the molecular structures *I—XIV* were carried out with application of a modified version of the standard MNDO program[22] which was extended by the possibility of calculations of sulphur-containing structures. The parametrization used was taken from ref.[23]. For the input approximation of the structure optimizations the idealized parameters were taken from ref.[24]. The optimization itself (with maintained fixed geometry of the benzene ring) concerned the —NCS (*I— VII*) and —CONCS (*VIII—XIV*) groups proper and the respective substituents X. The starting mutual orientations of the —NCS (—CONCS) group and phenyl ring were chosen in such way that their planes were deviated from each other by 5°.

The dipole moments were determined in benzene by usual procedures and by calculations according to Halverstadt & Kumler[25].

RESULTS AND DISCUSSION

Among the phenyl isothiocyanates the most studied structure was that of the parent non-substituted phenyl isothiocyanate *viz.* by means of IR, microwave, and Raman spectroscopy (refs[15–17,26–29]), the common features of these studies being spectral data consistent with linear arrangement of the —NCS group and (several times) suggestion of possible C_{2v} molecular symmetry. This many times accepted but questionable presumption[1] is based on the finding[30] that the dipole moment value of *p*-diisothiocyanatobenzene is equal to zero, although this finding does not exclude a non-linear arrangement of the C(4)—N=C=S fragment. The other geometrical parameters show smaller or greater differences (in the bond lengths and/or in the valence or dihedral angles), the molecular symmetries C_{2v}, C_1, and C_s being considered probable (with the dihedral angle 0° or 90°). The previous quantum-chemical calculations (MINDO) of phenyl isothiocyanate correspond well to the experimental results from microwave spectra which stand in accordance with the mesomeric structures *a—d* (Scheme 2)[28]. Our quantum-chemical calculations of structural parameters of phenyl isothiocyanates also agree well with the experimental values mentioned. The selected structural parameters obtained experimentally are summarized in

Table I along with our parameters obtained by the optimized MNDO calculation. The data given show that the geometry of phenyl isothiocyanate found by the MNDO method does not significantly differ from the experimental geometry. The values of the optimized bond lengths and C(4)NC angle correspond relatively well to the results of microwave spectra[28,29]. The single noteworthy difference concerns the non-linearity of —NCS group predicted by the MNDO method (the deviation from linearity is 8·8°).
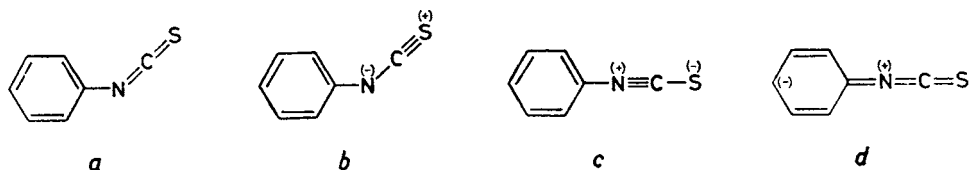
SCHEME 2

Substituents often have a distinct effect on structural parameters of molecules. So *e.g.* for *para* substituted anilines[31] it was found by the MINDO/3 that there is linear correlation between the angle formed by the extended connecting line C—N and the HNH angle axis and the σ_p constants. In the phenyl isothiocyanate series the effect of the substituent X makes itself felt in changes of bond lengths and bond angles. Although these changes are small, it can be seen that a transition from an electron-donor to an electron-acceptor substituent is connected with shortening of the C(4)—N and C—S bonds and diminishing of the C(4)NC and NCS bond angles and lenghtening of the N=C bonds. Consequently, the carbon–sulphur bond is rather a double bond, whereas the C—S bond is more or less (depending on the substituent) delocalized in the direction to the aromatic ring. This trend makes itself felt in lenghtening or shortening of C(4)—N bond. The changes mentioned are connected with the charge transfer from the —NCS group to the substituted phenyl fragment. As it follows from Table II the negative charge of —NCS group decreases in the sense mentioned, the sulphur atom being most engaged in this decrease (the increase of positive charge at the carbon atom of —NCS group is not so distinct). Interestingly, the bond length changes due to the X substituent are almost the same in the *para* series as in the *meta* series $(I - VII)$, the bond angles exhibiting a larger difference between a substituent effect in the *para* and *meta* substituted series. The decreasing C(4)NC and NCS bond angles in the trend mentioned are connected with increasing positive charge at carbon and decreasing negative charge at sulphur atom of the —NCS group and/or with increased orbital interaction between these atoms and the substituted phenyl residue. The non-linearity of the —NCS group is energetically advantageous also for substituted phenyl isothiocyanates. This conclusion is also supported by the crystallographical data[18] where the deviation from linearity is 4° for *p*-bromophenyl isothiocyanate. No experimental structural parameters

TABLE I

The structural parameters of *meta* and *para* substituted phenyl isothiocyanates and the respective dipole moments

The MNDO optimized calculation

X	Bond lengths, pm			Bond angles, °		Dipole moments[a]			Ref.
	C(4)—N	N=C	C=S	C(4)—N=C	N=C=S	μ_{exp}	μ_a	μ_{MNDO}	
p-N(CH$_3$)$_2$	139.8	120.8	151.4	149.0	171.2	—	13.86	14.15	—
p-Cl	139.8	121.1	151.1	147.5	170.9	5.17	5.25	6.46	—
p-NO$_2$	139.6	121.5	150.8	146.7	170.9	4.10	4.71	5.08	—
H	139.9	120.9	151.3	148.4	171.2	9.70	9.70	12.11	—
m-N(CH$_3$)$_2$	139.8	121.0	151.3	148.1	170.9	—	15.20	15.68	—
m-Cl	139.8	121.2	151.1	147.1	170.9	8.64	10.30	10.56	—
m-NO$_2$	139.6	121.5	150.8	146.1	170.7	—	15.30	15.05	—

The experimentally found (derived) parameters

X	Bond lengths, pm			Bond angles, °		Dihedral angle C(3)—C(4)—N=C, °	Ref.
	C(4)—N	N=C	C=S	C(4)—N=C	N=C=S		
H	140.0	121.6	156.1	145.0	180.0	0.0	28
H	137.0	121.6	156.0	148.0	180.0	0.0	29
H	—	—	—	—	180.0	90.0	17
H	—	—	—	—	180.0	non-planar arrangement	16
p-Br	138.0	115.0	154.0	153.6	176.0	0.0	18

[a] The experimental values according to ref.[20] in the values of 10^{-30} Cm.

are available for benzoyl isothiocyanates. The optimized bond lengths and angles of the non-substituted benzoyl isothiocyanate assume the values expected on the basis of the experimental values belonging to —NCS group and benzoyl residue. With substituted benzoyl isothiocyanates a transition from an electron-donor to electron-acceptor substituent results in the C(7)—N and C=S bond shortening and diminishing of the OCN and CNC angles as well as in an increase of C(4)—C(7), N=C, and C=O bond lengths and NCS bond angle. Interestingly, the OCN angle assumes a value comparable with the OCO(H) angle values obtained from the optimization of geometry (CNDO/2) of *meta* and *para* substituted benzoic acids[32,33]. With these derivatives $(VIII - XIV)$ it is noteworthy that the calculation provides the values about 90° for the C(5)—C(4)—C(7)=O dihedral angle in the *meta* substituted series. As the same values are obtained for the C(3)—C(4)—C(7)—N dihedral angle of these derivatives, the optimum arrangements of the phenyl group and —CONCS are placed in the planes which are almost mutually perpendicular (Scheme 3). Our previous papers dealing with dipole moments and ^{13}C NMR spectra of these derivatives[21,34] showed that the —CONCS group is a stronger electron acceptor than —NCS group, which is also indicated by the electronic charges at selected centres of the *meta* and *para* substituted phenyl and benzoyl isothiocyanates (Tables II and III) especially by the total charges of the C(4)—NCS and C(4)——CONCS fragments. The charge at C(4) seems to be decisive for estimation of these effects, being positive and negative in the phenyl and benzoyl isothiocyanates, respectively. The reason probably lies in the distinct positive charge at the carbon atom of carbonyl group of benzoyl isothiocyanates which is primarily compensated by negative charges at the adjacent atoms (N, O, C(4)). Plausibility of the non-linear arrangement of —NCS group within the —CONCS grouping follows − in this case − directly from the electron distribution and/or from the attractive interaction

TABLE II

The total electronic charges Q (in e) at selected atomic centres in the series of *meta* and *para* substituted phenyl isothiocyanates

X	$Q_{C(4)}$	Q_N	Q_C	Q_S	Q_{NCS}	$Q_{C(4)NCS}$
p-N(CH$_3$)$_2$	0·143	−0·309	0·246	−0·163	−0·226	−0·083
p-Cl	0·153	−0·312	0·247	−0·143	−0·208	−0·055
p-NO$_2$	0·183	−0·322	0·250	−0·115	−0·187	−0·004
H	0·143	−0·307	0·247	−0·162	−0·222	−0·079
m-N(CH$_3$)$_2$	0·140	−0·308	0·248	−0·159	−0·219	−0·079
m-Cl	0·150	−0·312	0·248	−0·140	−0·205	−0·054
m-NO$_2$	0·151	−0·318	0·249	−0·113	−0·182	−0·031

TABLE III

The structural parameters obtained by the optimized MNDO calculation for *meta* and *para* substituted benzoyl isothiocyanates

X	Bond lengths, pm					Bond angles, °			Dihedral angle, °
	C(4)—C(7)	C=O	C—N	N=C	C=S	O=C—N	C—N—C	N=C=S	C(5)=C(4)—C=O
p-N(CH$_3$)$_2$	149·8	121·8	141·9	121·1	151·0	118·5	150·4	188·0	8·1
p-Cl	150·3	122·2	141·7	121·4	150·8	118·1	147·8	188·3	3·1
p-NO$_2$	150·7	122·3	141·6	121·7	150·6	117·1	146·4	188·5	2·5
H	150·1	122·2	141·9	121·2	151·0	118·5	149·3	188·1	3·2
m-N(CH$_3$)$_2$	149·9	121·8	141·7	121·0	151·1	118·5	152·1	187·6	92·7
m-Cl	149·9	121·8	141·6	121·3	150·9	118·4	150·0	188·0	86·8
m-NO$_2$	150·1	121·9	141·6	121·7	150·6	118·4	147·6	188·3	85·6

TABLE IV

The total electronic charges Q (in e) at selected atomic centres and groupings in *meta* and *para* substituted benzoyl isothiocyanates

X	$Q_{C(4)}$	$Q_{C(7)}$	Q_O	Q_N	Q_C	Q_S	Q_{CONCS}	$Q_{C(4)CONCS}$	Q_{NCS}
p-N(CH$_3$)$_2$	−0·125	0·485	−0·304	−0·418	0·290	−0·141	−0·088	−0·213	−0·269
p-Cl	−0·116	0·477	−0·300	−0·419	0·288	−0·125	−0·079	−0·195	−0·256
p-NO$_2$	−0·089	0·469	−0·293	−0·422	0·287	−0·104	−0·063	−0·152	−0·239
H	−0·122	0·484	−0·303	−0·418	0·290	−0·139	−0·086	−0·208	−0·267
m-N(CH$_3$)$_2$	−0·111	0·491	−0·283	−0·420	0·294	−0·144	−0·062	−0·173	−0·270
m-Cl	−0·102	0·485	−0·280	−0·421	0·291	−0·127	−0·052	−0·154	−0·257
m-NO$_7$	−0·100	0·476	−0·275	−0·422	0·287	−0·104	−0·038	−0·138	−0·239
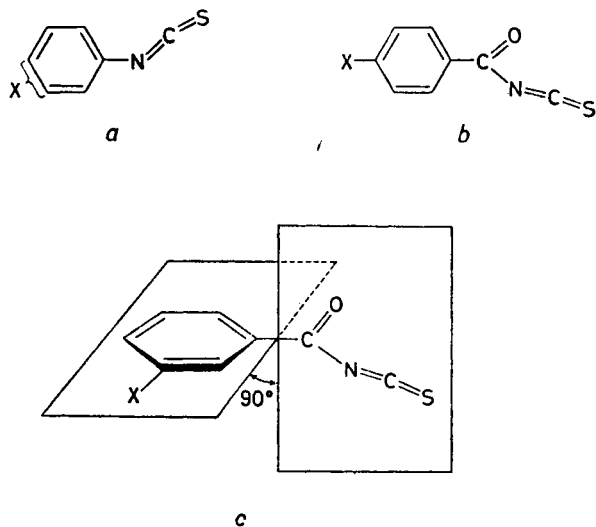
SCHEME 3

between the carbon atom of —NCS group and oxygen atom and from the repulsive interactions O...N and O...S. The relatively large positive charge at the C(7) atom probably also causes the CNC angle increase as compared with that of phenyl isothiocyanate.

Comparison of experimental values of dipole moments of benzoyl isothiocyanates with the values calculated by vector addition of the μ_a group moments carried out for the *syn* and *anti* conformers (Table V) also leads to the conclusion about non-

TABLE V

The dipole moments ($.10^{-30}$ Cm) of *meta* and *para* substituted benzoyl isothiocyanates[a]

X-*para*	μ_{exp}	μ_{MNDO}	μ_a	X-*meta*	μ_{exp}	μ_{MNDO}	μ_a
$N(CH_3)_2$	15·3	15·7	$15·1^b$	$N(CH_3)_2$	12·8	14·5	$13·4^c$
Cl	6·7	8·4	6·1	Cl	8·6	10·7	$11·0^d$
NO_2	5·5	6·6	4·2	NO_2	12·1	14·5	$15·1^e$
H	10·9	13·5	10·9	—	—	—	—

[a] The experimental values of the *para* substituted derivatives were taken from ref.[21]. The μ_a values are the dipole moments calculated by the vector addition of the group moments. Furthe; values for non-planar substituent X = $N(CH_3)_2$ and possible *syn* and *anti* conformers of thest *meta*-derivatives are: [b] 16·1; [c] 6·0, 8·2, 10·8; [d] 8·0; [e] 9·4.

-planar arrangement particularly in the *meta* substituted derivatives. The earlier analysis[21] based on a simple graphical method[25] already has suggested a similar conclusion. The dipole moments calculated by the MNDO method for compounds *I – XIV* agree — as expected — with the experimental values following the same trend, but the theoretical values are higher by about $1/4$.

In conclusion we can summarize the most important structural findings:

1) The MNDO calculation provides structural parameters which stand in good accordance with available experimental data (Table I) of phenyl isothiocyanates, their MNDO model corresponding to the model *a* (Scheme 3).

2) For benzoyl isothiocyanates the MNDO calculation provides the models represented in Scheme 3 with the respective optimized structural parameters (Table III).

REFERENCES

1. Wittel K., Meeks J. L., McGlynn S. P. in the book: *The Chemistry of the Cyanates and their Thio Derivatives* (S. Patai, Ed.), Chap. 1 .Wiley–Interscience, New York 1977.
2. Kniseley R. N., Hirschmann R. P., Fassel V. A.: Spectrochim. Acta *23*, 109 (1967).
3. Sakaizumi T., Ohashi O., Yamaguchi I.: Bull. Chem. Soc. Jpn. *49*, 948 (1976).
4. Tvaroška I., Gemeiner P., Drobnica Ľ.: Eur. J. Med. Chem. *16*, 131 (1981).
5. Kewley R., Sastry K. V. L. N., Winnewisser M.: J. Mol. Spectrosc. *10*, 418 (1963).
6. Lett R. G., Flygare W. H.: J. Chem. Phys. *47*, 4730 (1967).
7. Hargittai I., Paul I. C.: Ref.[1], Chap. 2.
8. Jenkins D. R., Kewley R., Sugden T. M.: Trans. Faraday Soc. *58*, 1284 (1962).
9. Dössel K.-F., Sutter D. H.: Z. Naturforsch. *34a*, 482 (1979).
10. Ebsworth E. A. V., Mays M. J.: J. Chem. Soc. *1962*, 4844.
11. Gerry M. C. L., Thompson J. C., Sugden T. M.: Nature *211*, 846 (1966).
12. Glidewell C., Robiette A. G., Sheldrick G. M.: Chem. Phys. Lett. *16*, 526 (1972).
13. Wasylishen R. E., Graham M. R., Danchura W.: J. Mol. Struct. *51*, 145 (1979).
14. Kimura K., Katada K., Bauer S. H.: J. Am. Chem. Soc. *88*, 416 (1966).
15. Stephenson C. V., Coburn W. C. jr, Wilcox W. S.: Spectrochim. Acta *17*, 933 (1961).
16. Ham N. S., Willis J. B.: Spectrochim. Acta *16*, 279 (1960).
17. El Shahawy A., Gaufres R.: J. Chim. Phys. *74*, 9 (1977).
18. Ulický L., Soldánová J.: Chem. Zvesti *39*, 473 (1985).
19. Bak B., Christiansen J. J., Nielsen O. J., Svanholt H.: Acta Chem. Scand., A *31*, 666 (1977).
20. Drobnica Ľ., Kristian P., Augustin J.: Ref.[1], Chap. 12.
21. Kristian P., Hritzová O., Talán P.: Collect. Czech. Chem. Commun. *42*, 671 (1977).
22. Dewar M. J. S., Thiel W.: J. Am. Chem. Soc. *99*, 4899, 4907 (1977).
23. Dewar M. J. S., McKee L. M., Rzepa H. S.: J. Am. Chem. Soc. *100*, 3607 (1978).
24. Pople J. A., Gordon M.: J. Am. Chem. Soc. *89*, 4253 (1967).
25. Exner O.: *Dipole Moments in Organic Chemistry*. Thieme, Stuttgart 1975.
26. Chantry G. W., Nicol E. A., Harrison D. J., Boucqy A., Roussy G.: Spectrochim. Acta, A *30*, 1717 (1974).
27. Bouchy A., Roussy G.: C. R. Acad. Sci., Paris C *277*, 143 (1973).
28. Higgins R. J., Combs L. L., Malloy T. B. jr, Cook R. L.: J. Mol. Struct. *28*, 121 (1975).

29. Onda M., Kambayashi S., Sakaizumi T., Yamaguchi I.: J. Mol. Struct. *34*, 299 (1976).
30. Antoš K., Martvoň A., Kristian P.: Collect. Czech. Chem. Commun. *31*, 3737 (1966).
31. Parr W. J. E., Wasylishen R. E.: J. Mol. Struct. *38*, 272 (1977).
32. Böhm S., Kuthan J.: Collect. Czech. Chem. Commun. *47*, 3393 (1982).
33. Böhm S., Kuthan J.: Collect. Czech. Commun. *48*, 1019 (1983).
34. Danihel I., Imrich J., Koščík D., Kristian P., Barančíková G.: Collect. Czech. Chem. Commun. *50*, 1422 (1985).

Translated by J. Panchartek.