Study of the structure of some *meta*- and *para*-substituted phenyl and benzoyl isocyanates by MNDO method

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It has been found on the basis of optimized MNDO calculations for a series of the *meta*- and *para*-substituted phenyl and benzoyl isocyanates that the —NCO group is nonlinear in both cases (deviation from linearity is about 13°). While the optimized bond lengths are in good agreement with the experimental values, the optimized values of the CNC valence angle are smaller than the experimental values. For some substituted benzoyl isocyanates the MNDO calculation leads to incorrect conformation of the —CONCO group with respect to phenyl rest. The values of overall positive charge and LUMO coefficients of electrophilic centres of benzoyl isocyanates enable us to estimate the selectivity with respect to nucleophilic agents.

Исходя из оптимализированных расчетов методом MNDO ряда *мета* и *пара* замещенных фенилизоцианатов и бензоилизоцианатов было найдено, что группа —NCO в обоих случаях нелинейна (отклонение от линейности представляет около 13°). В то время, как оптимализированные длины связей хорошо согласуются с соответствующими экспериментальными величинами, оптимализированные значения валентного угла CNC меньше экспериментальных величин. У замещенных бензоилизоцианатов расчет методом MNDO приводит для некоторых заместителей к неверной конформации группы —CONCO по отношению к фенильному остатку. На основании величин полных положительных зарядов и значений коэффициентов LUMO на электрофильных центрах бензоилизоцианатов можно судить об их селективности по отношению к нуклеофильным агентам.

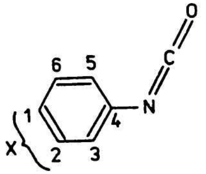
The study of the structure of isocyanates and especially of phenyl and benzoyl isocyanates, which are important representatives of this group of compounds, represents an interesting physicochemical problem from several points of view [1, 2]. It particularly concerns the points at issue in context with the values of the RNC and CNC valence angles, the linearity or nonlinearity of the —NCO group and the conformations of the —NCO and —CONCO groups with respect to the hydrocarbon rests of molecules.

For isocyanates like for isothiocyanates, the experimental data about the structure of a smaller number of derivatives are known from literature while no experimental parameters of the structure of acyl isocyanates and acyl isothiocyanates are available. Moreover, the experimental structural data obtained by the different physicochemical methods do not always lead to completely equal conclusions about the structure of isocyanates. For nonaromatic isocyanates the geometrical data determined in the gaseous phase may be summarized as follows: The values of the RNC valence angle are significantly different from 180° (they are within the range 119°—140°). SiH_3NCO is an exception for which the angle of 180° has also been quoted [3]. It is valid for the bond lengths that $r(N{=}C) > r(C{=}O)$, the mean values being 120.6 and 117.1 pm. The linearity (or nonlinearity) of the —NCO group is subject-matter of discussion. The possibility of nonlinear arrangement of the —NCO group is largely indicated by the conclusions resulting from the data of microwave spectra [4—6] and electron diffraction [7, 8] of ClNCO, CH_3NCO, and CH_3CH_2NCO for which the deviations from linearity vary within the range 8.6°—12.2°

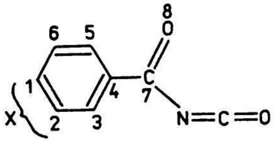
Important information about the structure of nonaromatic isocyanates is supplied by quantum-chemical studies [9—13] carried out by nonempirical and semiempirical methods. The CNDO/2 calculations of the Y—NCO substances (Y = H, Li, F, Cl) [9] indicate the YNC angle varying within the range 118.2°—134.8° and the nonlinearity of the —NCO group with a deviation of about 10°. The problem of the structure of nitrile isocyanate was also discussed. The interpretation of the infrared spectra of NCNCO [14] was based on linear arrangement of a molecule in the gaseous phase while nonlinear structure of a molecule with the internal NCN angle of 140° was assumed in the interpretation of microwave (MW) spectra [15]. The INDO calculation of this molecule also leads to a nonlinear structure with the internal NCN angle of 120° [10]. The case of silyl isocyanate is alike. The interpretation of the IR and MW spectra published earlier [3, 16] was consistent with linear structure of the SiNCO fragment, but the data obtained by electron diffraction suggested a nonlinear structure with the angle of 152° [17]. More recent microwave and vibration data [18, 19] indicate an energy minimum at about 158° The *ab initio* calculation of this compound [11] points to the energy minimum for the angle of 153°, which is in line with the mentioned experimental values. For ethyl isocyanate the *ab initio* calculation [6] indicates only one energy minimum with the $—CH_3$ group antiperiplanar with respect to —NCO, which is not in agreement with rotation as well as electron diffraction data according to which the stable conformer should have the $—CH_3$ group in synperiplanar position with respect to the —NCO group (like ethyl isothiocyanate [20]). For vinyl isocyanate the *ab initio* calculation [12] showed two stable conformations (in agreement with experiment [21]), *i.e.* planar *cis* and *trans* conformations. Without optimizing the geometry the *trans* conformer appeared to be preferable, but the calculation involving the optimized geometry preferred the *cis* conformer as the more stable. According to this calculation the nonlinearity of the —NCO group corresponds approximately to 10°.

As for aromatic isocyanates, only the structure of phenyl isocyanate was investigated by using the microwave [22—25] and Raman [26] spectra. It results from the determined values that the bond lengths and the valence angles are approximately equal to the corresponding values obtained for nonaromatic isocyanates. The molecule of phenyl isocyanate is planar and the determined values of the CNC angle (138.3° and 140.8°) are in good agreement with the value found by MINDO calculation (141°) [23]. The electron distribution was investigated for a small series of acyl isocyanates on the basis of CNDO/2 and *ab initio* calculations [27].

In our preceding studies [28, 29] we tried to use the MNDO method for investigating the structure of the *meta-* and *para-*substituted phenyl isothiocyanates and benzoyl isothiocyanates. We found that the optimized values of bond lengths and valence angles were in satisfactory agreement with available experimental structural parameters. However, the results of optimization in the scope of MNDO method led to an unexpected and improbable geometry of the molecules of the *meta-*substituted benzoyl isothiocyanates, *i.e.* to a nearly perpendicular arrangement of the plane of the —CONCS group with respect to the plane of aromatic ring. This statement as well as the interest in these problems from the standpoint of experimental organic chemistry [1, 2] stimulated us to investigate the optimized geometries of the *meta-* and *para-*-substituted phenyl and benzoyl isocyanates by using the MNDO method.



I—XV



XVI—XXX

X N(CH$_3$)$_2$, OCH$_3$, CH$_3$, H, F, Cl, CN, NO$_2$.

Calculations

The calculations of molecular structures *I—XXX* were carried out by using the modified version of the standard MNDO program [30] that was extended by the possibility of calculating the structures involving the elements of the third period. The applied parametrization was taken from paper [31] and the idealized parameters [32] were used as input approximation for optimizing the structures. The optimization itself concerned the proper —NCO (*I—XV*) or —CONCO (*XVI—XXX*) groups and the pertinent substituent X at a fixed geometry of benzene ring.

Table 1

Structural parameters obtained by the optimized MNDO calculations for some *meta*- and *para*-substituted phenyl isocyanates

X	Bond lengths/pm			Bond angles/°	
	C—N	N═C	C═O	C—N═C	N═C═O
p-N(CH$_3$)$_2$	141.0	124.8	118.4	130.9	193.7
p-OCH$_3$	141.0	124.8	118.4	130.5	193.6
p-CH$_3$	141.0	124.8	118.4	131.0	193.7
p-F	141.0	125.0	118.3	130.5	193.6
p-Cl	140.9	125.0	118.3	130.9	193.6
p-CN	140.8	125.1	118.2	130.6	193.7
p-NO$_2$	140.6	125.2	118.1	131.1	193.7
H	141.0	124.8	118.4	131.0	193.6
m-N(CH$_3$)$_2$	141.1	124.8	118.4	130.9	193.7
m-OCH$_3$	141.0	124.9	118.4	130.6	193.7
m-CH$_3$	141.0	124.8	118.4	131.0	193.7
m-F	140.9	124.9	118.3	130.9	193.7
m-Cl	140.9	125.0	118.3	130.6	193.8
m-CN	140.9	125.0	118.3	130.8	193.7
m-NO$_2$	140.7	125.2	118.1	130.9	193.8
Data derived from microwave spectra [22, 23, 25]					
H	137.0	120.7	117.1	140.6	180.0
H	140.0	120.7	117.1	138.3	180.0
H	137.0	120.7	117.1	140.8	180.0

Results and discussion

The structural parameters of the substituted phenyl isocyanates obtained by the optimized calculations on the basis of MNDO method are presented in Table 1. As for aromatic isocyanates, only the data about phenyl isocyanate are available in literature. These data were deduced from microwave spectra [22, 23, 25]. A confrontation of the experimental values with the values obtained by the optimized MNDO calculation shows (Table 1) that the calculated bond lengths are somewhat longer while the CNC valence angles are smaller than the experimental ones. Like in the substituted phenyl isothiocyanates [28, 29], the C—N and C═O bond lengths are reduced and the N═C bond lengths are extended by passing from electron donor to electron acceptor substituents of phenyl isocyanates. However, these changes are smaller than those in the substituted phenyl isothiocyanates. The bond angles change only a little and we cannot observe an analogous change like in phenyl isothiocyanates which consists in reduction of the CNC and NCS angles in the above-mentioned line. As expected, the values themselves of the CNC valence angle are smaller than those observed for phenyl isothiocyanates [1, 2], but rather small when compared with the values obtained from microwave spectra (difference of about 9°) [22, 23, 25]. The agreement is better for phenyl isothiocyanate (calculated 148.4°, found by experiment 148.0° and 145.0° [23]). A similar difference in the values of the HNC and CNC valence angles was also observed for isocyanic acid and methyl isocyanate, the experimental values being equal to 130.2° and 140.3° and the calculated ones being equal to 117.9° and 128.1° [33—35]. The *ab initio* calculation of isocyanic acid [13] gives more consistent results (124°).

A relatively small value of the CNC valence angle determined by the MNDO calculation when compared with the experimental value may be due to the estimation of the interactions between the —NCO group and phenyl rest, especially among the C atom of the —NCO group and carbons which are in *ortho* and *ipso* position with respect to it and the hydrogen atom in *ortho* position. It is worth noticing that the decrease in value of the optimized CNC angle of phenyl isocyanate when compared with phenyl isothiocyanate corresponds to the increase in the attractive (A) coulombic interaction between C-5 and C with respect to the repulsive (R) coulombic interaction between C-4 and C or H in *ortho* position and C. The ratio A/R is 0.52 for phenyl isocyanate and 0.40 for phenyl isothiocyanate. The evaluation of the attractive and repulsive interactions of other substituted phenyl isocyanates and phenyl isothiocyanates points out equal relation of them to magnitude of the CNC angle as observed for nonsubstituted phenyl isocyanate and phenyl isothiocyanate.

A possible nonlinearity of the —NCO group is suggested not only by quantum-chemical calculations [9—13] but also by the data resulting from microwave spectra and electron diffraction [4—8]. According to MNDO calculations the deviation from linearity of the —NCO group in phenyl isocyanate is about 13.6°. The overall energy of phenyl isocyanate with linear arrangement is by 10.25 $\mathrm{kJ\,mol^{-1}}$ greater.

From the viewpoint of electron distribution in phenyl isocyanates the value of positive charge on the carbon atom of the —NCO group (Table 2) is remarkably high in comparison with the corresponding value of phenyl isothiocyanates. Nevertheless, it is in line with the results of kinetic measurements [36] according to which the rate of nucleophilic addition to the carbon atom of the —NCO group is significantly higher than that of the addition to the carbon atom of the —NCS group.

The fact that the optimization of geometry in the MNDO calculations does not involve the benzene ring of the investigated compounds has no influence on the presented conclusions. The calculations performed for a limited set of substituted phenyl isocyanates with optimization of whole molecules give identical results as regards structural parameters of the —NCO group (Table 1) and electron distribution in this group (Table 2).

Table 2

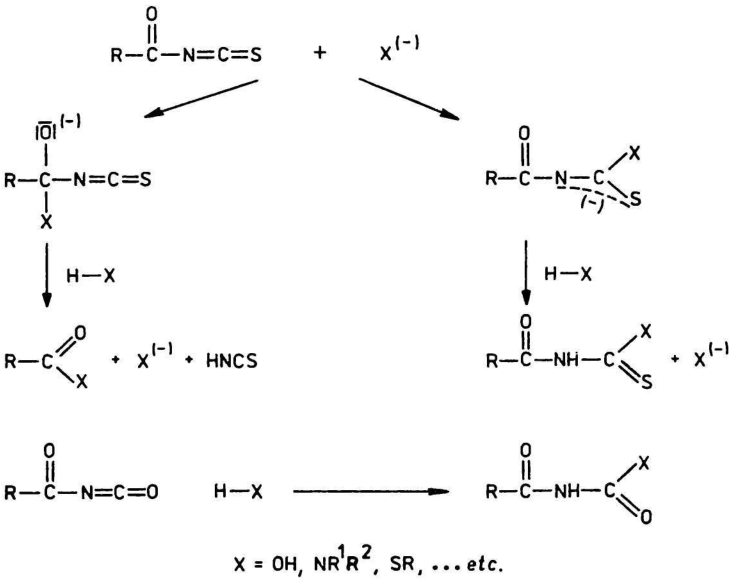
Overall electron charge (Q/e) on the atoms of functional groups of some selected *meta*- and *para*-substituted phenyl isocyanates and benzoyl isocyanates

X	Phenyl isocyanates			Benzoyl isocyanates				
	Q_N	Q_C	Q_O	$Q_{C\text{-}7}$	$Q_{O\text{-}8}$	Q_N	Q_C	Q_O
p-OCH$_3$	−0.334	0.395	−0.202	0.446	−0.349	−0.440	0.451	−0.187
p-F	−0.335	0.397	−0.192	0.442	−0.341	−0.442	0.454	−0.180
p-CN	−0.338	0.404	−0.186	0.437	−0.337	−0.443	0.455	−0.175
H	−0.335	0.397	−0.200	0.442	−0.344	−0.440	0.452	−0.187
m-OCH$_3$	−0.334	0.396	−0.208	0.442	−0.339	−0.440	0.452	−0.186
m-F	−0.335	0.397	−0.191	0.441	−0.338	−0.441	0.454	−0.181
m-CN	−0.338	0.401	−0.180	0.440	−0.336	−0.443	0.457	−0.172

There are not available any experimental structural parameters of benzoyl isocyanates. The optimized bond lengths and valence angles of the nonsubstituted benzoyl isocyanate assume the values which should be expected on the basis of the experimental values belonging to the —NCO group and benzoyl rest. Thus the following values (in pm) are valid for the nonsubstituted benzoyl isocyanate: C-4—C-7 150.5; C-7═O 122.7; C—N 141.9; N═C 125.0; C═O 118.1; OC-7N 118.4°; CNC 132.1°; NCO 192.6° The effect of the transition from electron donor to electron acceptor substituent consists in the fact that the bond lengths and valence angles change only very little and this influence of substituents is smaller when compared with their influence on those properties of the substituted benzoyl isothiocyanates [28, 29]. The influence of substituent X does not practically manifest itself in the bond lengths C-7═O, C-7—N, C═O and in the NCO valence angle. A more conspicuous effect of substituent is reflected in the C-4—C-7 and N═C bonds which are extended from 150.1 to 150.9 pm and from 125.0 to 125.3 pm, respectively as well as in the OC-7N angle which increases from 118.3° to 119.1°. In comparison with benzoyl isothiocyanates the optimized OC-7N angles are almost equal while the CNC angle of benzoyl isocyanates is much smaller (approximately by 17°) and the deviation from linear arrangement is greater for the —NCO group than for the —NCS group of benzoyl isothiocyanates (12.6° and 8.1°).

For the majority of the X-substituted benzoyl isocyanates the MNDO calculations at a fixed geometry of benzene ring show that the —CONCO group is practically in one plane with the benzene ring. For some derivatives (X = N(CH$_3$)$_2$ or NO$_2$) the calculations, however suggest that the conformation of these molecules is analogous to that of the *meta*-substituted benzoyl isothiocyanates [28, 29], *i.e.* the —CONCO group is almost perpendicularly orientated with respect to the benzene ring. The calculations involving optimization of whole molecules, which were carried out with a small selected set of benzoyl isocyanates, also suggest conformations with almost perpendicular arrangement of the plane of the —CONCO group with respect to the plane of the benzene ring even for a nonsubstituted derivative. It is interesting to mention in this context that the EHT calculation, which frequently predicts correct conformational arrangement, attributes the energy minimum of rotation about the C-4—C-7 bond of benzoyl isocyanate to the 30° angle of angular displacement of the planes under consideration. A nearly perpendicular arrangement of the benzene ring and —CONCO group planes is improbable. It is known that the conformations of molecules predicted on the basis of semiempirical methods (CNDO/2, INDO) are different from the conformations determined from experimental data in some cases [37—40]. This discordance resulting from the considered semiempirical methods is to be attributed to underestimation of the contributions of two-centric components to overall energy which express the bonding contributions for planar conformations as well as to overestimation of the interactions between orbitals (especially π^* antibonding) since the contributions of these interactions assume their maximum value in nonplanar arrangement of interacting orbitals with consequent overestimation of nonplanar conformers.

The electron distribution in molecules of benzoyl isocyanates has also been a topic of our interest mainly because of reactivity of these compounds. It is known [41] that benzoyl isocyanates (acyl isocyanates) are much more reactive than phenyl isocyanates. They can react with electrophilic agents through their nucleophilic centres (nucleophilic centres O and N with lone electron pairs) as well as with nucleophilic agents (carbon atoms of the carbonyl and isocyanate group work as electrophilic centres). The obtained results show that benzoyl isocyanates like phenyl isocyanates are significantly more reactive than their sulfur analogues, especially with respect to nucleophilic agents. This assumption has been verified experimentally and is in harmony with the values of positive charge on carbon atoms of the carbonyl and isocyanate group (see also the CNDO/2 and *ab initio* calculations performed for some selected acyl isocyanates [27]). But the difference between the values of positive charge on carbon atoms of the carbonyl and isocyanate group of benzoyl isocyanates is very small (Table 2), which is remarkable in reference to benzoyl isothiocyanates. It results from these facts that benzoyl isocyanates are less selective to nucleophilic agents than benzoyl isothiocyanates. It is known [42, 43] that the nucleophilic agents attack not only the carbonyl carbon with a greater positive charge but also the carbon atom of the —NCS group of benzoyl isothiocyanates while benzoyl isocyanates yield with nucleophilic agents the addition products involving the carbon atom of the —NCO group [44], *i.e.* the derivatives of *N*-acylcarbamic acid (Scheme 1). For methoxycarbonyl isothiocyanate it has been derived on the



Scheme 1

basis of the CNDO/2 values of electron charge and electron densities in the frontier LUMO orbital [45] that the hard nucleophiles are prone to attack the carbonyl carbon atom while the soft nucleophiles attack the carbon atom of the —NCS group. The MNDO calculations for benzoyl isothiocyanates result in equal conclusion [29]. However, these calculations made with benzoyl isocyanates point out that the carbon atom of the —NCO group is a harder electrophilic centre ($c_{\text{LUMO}}^2 = 0.0604$) than the carbonyl carbon atom ($c_{\text{LUMO}}^2 = 0.1528$). Irrespective of the fact that the molecules of benzoyl isocyanates exhibit pronounced negative charge on nitrogen and oxygen atoms, these nucleophilic centres are not operative in reactions of benzoyl isocyanates with particular electrophiles.

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