# Joint Norwegian – Soviet Electron Diffraction Studies of Molecular Structures in the Gas Phase. I. Organic Compounds

Lev V. Vilkov, Vladimir S. Mastryukov, Mikhail V. Popik and Nina I. Sadova

Department of Chemistry, Moscow State University, Moscow 119899, USSR

Vilkov, L. V., Mastryukov, V. S., Popik, M. V. and Sadova, N. I., 1988. Joint Norwegian – Soviet Electron Diffraction Studies of Molecular Structures in the Gas Phase. I. Organic Compounds. – Acta Chem. Scand., Ser. A 42: 563–570.

A summary review of joint Norwegian–Soviet electron diffraction studies undertaken during the 17 years since 1971 is given. The conformational compositions and internal rotation potentials of benzyl chloride and bromide, a number of dienes (isoprene, α-chloroacrolein and divinyl ketone), cyclic hydrocarbons and silicon derivatives are considered. Using nitro derivatives of chloro- and bromobenzenes as examples, the effects of mutual influence of substituents via the ring are analyzed. The relations between mean amplitudes of vibration of the CC and CH atomic pairs and corresponding internuclear distances have been determined.

Dedicated to Professor Otto Bastiansen on his 70th birthday

## A common introduction to two parts

The Norwegian electron diffraction group is a classic one with respect both to experimental techniques and to its attitude to stereochemical issues. In the Soviet Union, electron diffraction studies were initiated much later, in the 1950's. As is often the case the younger team, while in many respects following the classical pattern, has also been trying new ways of its own.

The method of gas-phase electron diffraction is a complex combination of measurement, data processing and structure analysis techniques. Within this method, the structure problem is solved by stages, and this presupposes a natural division of labour realised in the first joint works: experiments and data processing have been performed at Moscow State University, while the amplitudes of vibration have been calculated at Trondheim. Stereochemically, these studies have merely been an extension of Norwegian works on four-membered ring conformations (vide infra).

The introduction of computers was a very important step in the development of the gas-phase electron diffraction method, for it enabled more complex structures to be solved with high accuracy. One of the first versatile programmes for electron diffraction data processing and least-squares treatment was written by Norwegian scientists.

Close cooperation of our teams dates from prof. O. Bastiansen's visit to Moscow in 1970. Prof. Bastiansen kindly provided us with new programmes for treating electron diffraction patterns.

At that time a new high-temperature technique for gas-phase electron diffraction studies of inorganic compounds such as metal halides, oxides, and salts of oxy acids had been developed at Moscow State University. This created a new basis for collaboration.

Friendly relations between Norwegian and Soviet electron diffractionists have been reinforced by mutual visits of scientists, and long-term work in Norway of A. A. Ischenko and M. V. Popik, each of whom had visited Oslo for 10 months, in 1976 and 1981, respectively.

Our cooperation has not only been fruitful from the point of view of scientific results but also rich in pleasant personal intercourse.

The electron diffraction laboratory of Moscow State University includes two groups working on organic and inorganic compounds, respectively, and for this reason the review consists of two

parts, the present paper, on organic compounds, constituting the first of these.

Contacts between Norwegian and Soviet electron diffractionists have grown into a cooperation as a result of similar scientific interests. This cooperation did not always take the form of joint publications: sometimes the two teams just worked on structurally related compounds. Such works will also be covered in the present review.

Chronologically, the first paper authored by Norwegian and Soviet scientists was that by Cyvin et al.[1] on vibrational effects in silacyclobutanes. Further cooperation has been developing in the following directions:

1. Conformations of acyclic, cyclic and heterocyclic compounds.

2. Aromatic compounds.

3. Amplitudes of vibration.

Norwegian participants in this work were A. Almenningen, B. N. Cyvin, S. J. Cyvin, J. Brunvoll and S. Samdal, who might rightfully be co-authors of the present review.

## Conformations of acyclic, cyclic, and heterocyclic compounds

*Conformations of benzyl halide molecules.* A structural study of $C_6H_5CH_2Cl$ and $C_6H_5CH_2Br$ was undertaken jointly by Soviet, Norwegian and Hungarian scientists[2] to gain information on rotation about the $C_{Ph}$–C bond.

The barrier to rotation about the $C_{Ph}$–C $\underset{\diagdown}{\diagup}$ type bond is lower than those for ethane and its

*Table 1.* The principal geometrical parameters of $C_6H_5CH_2Cl$ and $C_6H_5CH_2Br$ ($r^a$ in Å, angles in degrees).

| Parameters | $C_6H_5CH_2Cl$ | $C_6H_5CH_2Br$ |
|---|---|---|
| C–C | 1.402 (3) | 1.409 (9) |
| $C_{Ph}$ – C | 1.535 (10) | 1.528 (27) |
| C–X (X=Cl, Br) | 1.802 (6) | 1.978 (8) |
| CCX (X=Cl, Br) | 109.4 (1.6) | 110.0 (1.7) |
| φ average[a] | 67.5 (4.5) | 74.2 (1.3) |

[a] φ = 0° for the configuration with the C–Cl (Br) bond in the benzene ring plane.

derivatives, and the introduction of comparatively bulky substituents can significantly affect the potential function shape.

First, electron diffraction patterns of benzyl chloride and bromide have been analysed on the assumption of a Gaussian distribution of interatomic distances $(r_a)$ (Table 1). The $C \doteq C$ bond lengths in the benzene ring and the CCCl and CCBr valence angles are the same as in similar compounds. A comparison of the $r$(C–Cl) and $r$(C–Br) values found using the microwave data on $C_2H_5Cl$ [1.7785(3) Å³] and $C_2H_5Br$ (1.9400 Å³) shows these bonds to be elongated considerably under the influence of the benzene ring. The mean rotation angle value is about 70°.

We have been able to solve the internal rotation problem thanks to Brunvoll, who has calculated the amplitudes of framework vibrations, $l_{fr}$, from spectroscopic data.[5] The calculated amplitudes were approximately half as large as the experimental ones found on the assumption of a Gaussian distribution of internuclear distances $r_a$. This is indicative of a shallow internal rotation potential minimum. In Ref. 2, internal rotation has been included via the Boltzmann factor $e^{-V(\varphi)/RT}$ where the function $V(\varphi)$ is defined as $V(\varphi) = (V_2/2)$ [1-cos2$(\varphi - \varphi_0)$]. A symmetrical $(C_s)$ model with $\varphi_0 = 90°$ was refined to obtain $V_2 = 6.3 \pm 2.1$ kJ mol⁻¹ (1.5±0.5 kcal mol⁻¹) for $C_6H_5CH_2Cl$ and 8.3±2.1 kJ mol⁻¹ (2.0±0.5 kcal mol⁻¹) for $C_6H_5CH_2Br$.*

More recently, the $V(\varphi)$ functions and the barriers, to rotation for benzyl chloride and bromide have been refined using non-parametric potential functions.[6] New procedures for solving "poorly defined problems" have been applied to the Fredholm equation of the first kind arising in electron diffraction, as follows.

Suppose we can separate internal rotation from small-amplitude vibrations. The general equation for the reduced contribution to scattering intensity then takes on the integral form

$$sM(s) = \int_0^{2\pi} W(\varphi) \, sM(s, \varphi) \, d\varphi \qquad (1)$$

where $s = 4\pi/\lambda$ sin θ/2, λ is the wave length, θ the angle of electron scattering, $W(\varphi)$ the probability density for the angle φ, and $sM(s, \varphi)$ the

*1 cal = 4.184 J.

564

theoretical expression for the reduced intensity at a fixed value of the angle $\varphi$.

The $W(\varphi)$ function can to a good approximation be described by a Boltzmann distribution:

$$W(\varphi) = N \exp\left(-V(\varphi)/kT\right) \qquad (2)$$

where $V(\varphi)$ is the internal rotation potential function, and $N$ is the normalisation factor.

The function $sM(s,\varphi)$ is in fact the reduced intensity for the molecular frame as given by eqn. (3), where $l_{\mathrm{fr}\,ij}(\varphi)$ is the vibrational amplitude for a pair of frame atoms, $i$ and $j$, $r_{ij}(\varphi)$ is the interatomic distance [$r_{ij}(\varphi)$ and $l_{ij}(\varphi)$ depend on $\varphi$], and $g_{ij}(s)$ is the scattering factor.

The $r_{ij}$ values for bonded distances and the valence angle values can be determined at a preliminary structure analysis stage on the level of the small-amplitude vibration approximation. If the force field for the frame and therefore the $l_{\mathrm{fr}\,ij}(\varphi)$ values are also known, eqn. (1) is a Fredholm equation of the first kind with a known nucleus and $sM(s)_{\mathrm{exp.}}$ as the left-hand side.

However, a stable solution can only be found using special regularisation techniques. The function $W(\varphi)$ is determined from the experimental $sM(s)_{\mathrm{exp.}}$ values using known $r_{ij}$ bond distances, valence angles and $l_{\mathrm{fr}\,ij}(\varphi)$ amplitudes by the minimisation of the function

$$\min\left\{\Phi_\alpha[W(\varphi)] = \right.$$

$$\int_{S_{\min}}^{S_{\max}} \left[\int_0^{2\pi} W(\varphi)\, s\, M_{\mathrm{theor}}(s,\varphi)\, \mathrm{d}\varphi - s M_{\mathrm{exp}}(s)\right]^2 \mathrm{d}s$$

$$\left. + \alpha \int_0^{2\pi} \left[W^2(\varphi) + \left(\frac{\mathrm{d}\,W(\varphi)}{\mathrm{d}\varphi}\right)^2\right] \mathrm{d}\varphi\right\} \qquad (4)$$

where $\alpha$ is a numerical parameter ($\alpha > 0$). Solutions to eqn. (4) converge uniformly to the solution to eqn. (1). The function $W(\varphi)$ is obtained as a set of discrete $W_i$ values corresponding to $\varphi_i$ angles taken at intervals of $\Delta\varphi$ (10°). The parameter $\alpha$ is chosen by trial and error in such a way that the first term in eqn. (4) corresponds to ex-
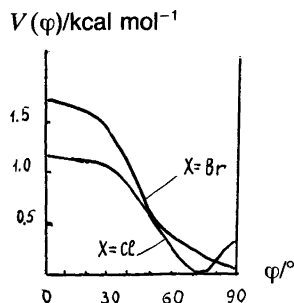


Fig. 1. The internal rotation potential functions for benzyl bromide and chloride.
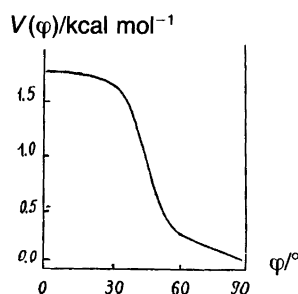


Fig. 2. The internal rotation potential function for benzyl chloride obtained with the condition that it must not increase.

perimental errors in $sM(s)_{\mathrm{exp.}}$ as estimated in previous least-squares reinements on semi-rigid models, and is generally found to be of the order of $10^{-3}$.

A priori characteristics of the probability density functions for benzyl chloride and bromide employed on the calculations were that it should be positive for all values of $\varphi$, have a positive second derivative in the range $0° < \varphi < \theta$ and a negative second derivative for $\theta < \varphi < 90°$. The point of inflection ($\theta$) was one of the refinement variables, and the optimum values found were close to 45°. The internal rotation potential functions are shown in Fig. 1. The function satisfying the additional requirement of monotonic decrease of the probability density function also gave good agreement with experiment (see Fig. 2).

$$sM(s,\varphi) = \sum_{i\neq j} g_{ij}\, \frac{\sin s\, r_{ij}(\varphi)}{r_{ij}(\varphi)} \exp\left(-s^2 l^2_{\mathrm{fr}\,ij}(\varphi)/2\right) \qquad (3)$$

In the electron diffraction study of $C_6H_5CH_2F$ performed by Trætteberg et al. in 1979[7] the angle $\varphi$ was found to be 52.3° with a 7° mean vibrational amplitude.

Among more recent works on the same problem, Refs. 8 and 9 should be mentioned. In the latter reference, the NMR spectrum of benzyl chloride is reported and the barrier to rotation is calculated by the SCF MO LCAO method using an STO-3G basis set with geometry optimisation. According to this work the conformation with the C–Cl bond normal to the ring plane is favoured energetically, the barrier to rotation being equal to 2.1 kcal mol$^{-1}$. This agrees with our estimate within the experimental uncertainties.

*Conformations of diene molecules.* Classical conjugated systems such as dienes are characterized by a planar *anti* arrangement of multiple bonds in most simple molecules, of which the first is butadiene, $CH_2=CH-CH=CH_2$.[10,11] Norwegian scientists have, however, shown that steric repulsions can render a conjugated system of multiple bonds non-planar, as e.g. in biphenyl and its derivatives.[12,13]

In the 1960's, we undertook a statistical analysis of structural data on diene derivatives, and found that the central C–C bond length is independent of the angle of rotation of multiple bond planes.[14] Later, we determined the structures of isoprene, $CH_2=C(CH_3)-CH=CH_2$,[15] α-chloroacrolein, $CH_2=CCl-CH=O$[16a] and divinyl ketone, $(CH_2=CH)_2C=O$.[17a] These compounds were chosen because the presence of substituents such as $CH_3$, Cl and $CH=CH_2$ can result in steric repulsions destabilising the *anti* arrangement of double bonds.

It was shown experimentally that the $CH_3$ group had no destabilising action. This conclusion has been confirmed in a more recent study of isoprene.[18] The presence of chlorine and the vinyl group as substituents on the C=C–C=O chain, however, causes an increase in the fraction of the $CH_2=CCl-CH=O$ isomer with a *syn* arrangement of double bonds[16b] and results in *syn,syn* and *syn,anti* conformations of $(CH_2=CH)_2$ C=O.[17a] The *anti,anti* conformer is practically absent in divinyl ketone.

It is of interest that *ab initio* calculations predict a planar *syn,syn* configuration for the divinyl ketone molecule.[17b] The *syn,anti* form has 1.8 kcal mol$^{-1}$ more energy.
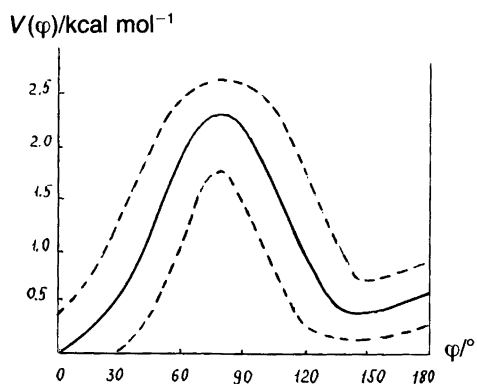
566

$V(\varphi)/\text{kcal mol}^{-1}$



*Fig. 3.* The internal rotation potential function (solid line) for α-chloroacrolein. The dotted lines correspond to experimental uncertainty.

Using the regularisation technique we have calculated $V(\varphi)$ on the basis of $l_{fr}$ amplitudes of vibration for the *syn* and *anti* configurations of α-chloroacrolein. At intermediate conformations, the amplitudes have been estimated by interpolation. The rotation potential function, $V(\varphi)$, for α-chloroacrolein is shown in Fig. 3. It has minima at $\varphi = 0°$ [$V(0°) = 0$ kcal mol$^{-1}$] and $\varphi = 135°$ [$V(135°) = 0.38$ kcal mol$^{-1}$]. The barriers to rotation are $V(80°) = 2.38$ and $V(180°) = 0.52$ kcal mol$^{-1}$.

*Conformations of four- and five-membered heterocyclic compounds containing silicon.* A study of cyclobutane by Norwegian scientists in 1960[19] showed the ring to be non-planar. Monohalogenated cyclobutanes occur as equilibrium mixtures of axial and equatorial forms.[20] We have extended the study of substituted cyclobutanes to silacyclobutane $(CH_2)_3SiH_2$[21] and dichlorosilacyclobutane $(CH_2)_3SiCl_2$.[22] The molecules have non-planar structures with the puckering angle close to that in cyclobutane.

In acyclic element derivatives and in the absence of effects of special kinds, bond configurations are rather easy to predict. With cyclic compounds the situation is more complex: for example, in four-membered rings the distribution of valence angles depends on ring bond lengths. Simplified molecular mechanics calculations have shown that this dependence can rather easily be utilised to estimate the angles in four-membered heterocyclic compounds.[23]

In silacyclobutanes there is a substantial widening of the CCC bond angle, to ca. 100° from 89° in

cyclobutane, and a strong puckering of the sila-cyclobutane ring can result from that widening since the torsion strain about the C–C bond for the eclipsed conformation then increases.

Formally, cyclopentane is the simplest five-membered cyclic system. Its conformation can, however, only be analysed in terms of the "pseudorotation" model. The introduction of substituents hinders or totally destroys pseudo-rotation,[24] an envelope or a half-chair conformation being favoured.
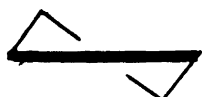


envelope          half chair

Seip's molecular mechanics calculations[25] show that the half-chair conformation is energetically favoured in silacyclopentane, $(CH_2)_4SiH_2$. This prediction has been confirmed by our study taking vibrational effects into consideration.[26] Thus silacyclopentane has been shown to be conformationally analogous to germacyclopentane, cyclopentanone, tetrahydrothiophene and tetrahydroselenophene, all of which were studied earlier (for references, see Ref. 26).

*The conformations of cyclic hydrocarbons.* Traditionally, the conformations of cyclic hydrocarbons have been the focus of interest of Norwegian researches; suffice it to mention the classic works by Bastiansen and co-workers on cyclobutane, cyclopentane, cyclohexane, and cyclooctane. Our interest in these systems arose in studying the four-[21,22] and five-membered[26] rings of silicon heterocyclic compounds (see above).

The first joint publication on cyclic hydrocarbons was that on dicyclobutylidene **1**.[27] The rings in **1** found to be flatter than that in cyclobutane (the dihedral angles in **1** and in cyclobutane are ~17 and ~26°, respectively).
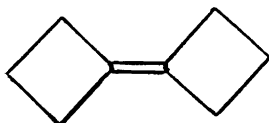


**1**

These results were not obtained in a joint work proper, for the fact that the same compound had been under study in the two laboratories was only recognized during Mastryukov's visit to Norway (1979) after the structure analysis had been completed both in Oslo and in Moscow. The published paper is therefore in fact a comparison of independently obtained results. Such undertakings are exceedingly useful methodologically, for they enable possible systematic errors and differences in computational procedures to be revealed. Earlier, similar work had been done on $1,12\text{-}C_2I_2B_{10}H_{10}$.[28,29] This compound was studied experimentally in Oslo and in Moscow. The structure analysis was performed at Moscow State University.

These works brought the scientific interests of the two teams still closer, and in the 1980's investigation of the following molecules was initiated:
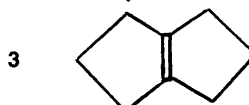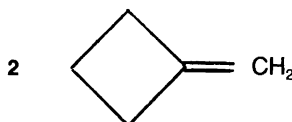


**5** $C_8H_{16}$ cyclooctane
**6** $C_9H_{18}$ cyclononane
**7** $C_{12}H_{24}$ cyclododecane

Electron diffraction patterns of all these compounds have been obtained in Oslo. Additional information employed in the structure analysis of these results includes:

(i) vibrational amplitudes and shrinkage corrections,

(ii) theoretical calculations on the geometrical structure of the molecule (*ab initio* calculations for **2**[30] and molecular mechanics calculations for compounds **3–7**).

567

*Table 2.* Gas-phase electron diffraction structure parameters for halogenated aromatic compounds (bond lengths, $r_g$, in Å, bond angles in degrees).

| Compound | C–C | C–NO$_2$ | N=O | C–X (X=Cl, Br) | ∠ONO | ∠CC$_{NO_2}$C | ∠CC$_X$C | $\varphi_{NO_2}$ | Ref. |
|---|---|---|---|---|---|---|---|---|---|
| $o$-ClC$_6$H$_4$NO$_2$ | 1.387 (2) | 1.462 (12) | 1.226 (2) | 1.721 (3) | 123.6 (1.0) | 121.3 (1.2) | 121.6 (0.7) | 34 (3) | 39a |
| $m$-ClC$_6$H$_4$NO$_2$ | 1.383 (3) | 1.442 (10) | 1.243 (3) | 1.746 (6) | 122.6 (1.0) | 123.0 (1.5) | 121.5 (1.5) | 13 (6) | 38a |
| $p$-ClC$_6$H$_4$NO$_2$ | 1.388 (3) | 1.469 (13) | 1.237 (3) | 1.707 (4) | 123.0 (0.9) | 122.6 (1.1) | 120.5 (0.6) | 19 (5) | 40 |
| 2,6-(NO$_2$)$_2$C$_6$H$_3$Cl | 1.395 (3) | 1.447 (4) | 1.229 (2) | 1.712 (5) | 123.0 (0.3) | 121.6 (0.4) | 118.9 (0.6) | 54 (1) | 39b |
| $o$-BrC$_6$H$_4$NO$_2$ | 1.386 (3) | 1.494 (14) | 1.218 (3) | 1.894 (6) | 128.6 (1.5) | 120.4 (2.4) | 119.6 (1.2) | 43 (3) | 38b |
| $m$-BrC$_6$H$_4$NO$_2$ | 1.394 (3) | 1.448 (14) | 1.238 (3) | 1.865 (8) | 121.8 (1.4) | 121.4 (1.5) | 121.4 (1.0) | 25 (5) | 38b |
| $p$-BrC$_6$H$_4$NO$_2$ | 1.399 (3) | 1.455 (12) | 1.240 (4) | 1.895 (7) | 125.0 (0.7) | 121.6 (0.6) | 122.6 (0.6) | 19 (3) | 37 |
| 2,6-(NO$_2$)$_2$C$_6$H$_3$Br | 1.393 (3) | 1.468 (9) | 1.229 (3) | 1.899 (9) | 125.6 (0.9) | 122.7 (0.9) | 117.1 (1.2) | 58 (3) | 38b |
| C$_6$H$_5$Cl | 1.400 (1) | – | – | 1.737 (6) | – | – | 121.7 (0.6) | – | 41 |
| C$_6$H$_5$Br | 1.396 (3) | – | – | 1.899 (3) | – | – | 121.4 (0.6) | – | 36 |

At present, preliminary results for **2**[30] and final results for **5**[31] have been published. The predominant conformer in **5** is the boat-chair.

One more problem of interest to both teams is that of bicyclo[3.1.0]hexane, **8**, occurring as a boat conformer.[32] Our work has been succeeded by *ab initio* calculations[33] and by the work of Trætteberg *et al.*,[34] who have shown two chlorinated derivatives **9** and **10** to possess different ring conformations, namely boat (**9**) and chair (**10**).
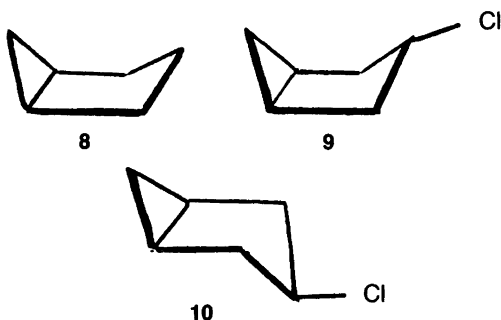


Yet another example is the study of cyclononane, which has, to a considerable degree, been based on the NMR results obtained by Krane (Trondheim University) during his visit to the USA.[35]

## Aromatic derivatives

Studies of bromobenzene[36] and $p$-nitrobromobenzene[37] have been performed as part of work on aromatic nitro compounds and halobenzenes. So far, structural data on $o$-, $m$- and $p$-NO$_2$C$_6$H$_4$X (X = Cl, Br) and 2,6-(NO$_2$)$_2$C$_6$H$_3$X (X = Cl, Br) have been reported (Table 2).

In nitrobenzene derivatives, the structural manifestations of mutual influence of the nitro group and the other benzene ring substituent are of major interest. A considerable (up to 0.03 Å) shortening of C–Cl bonds relative to chlorobenzene[41] has been observed for $o$-ClC$_6$H$_4$NO$_2$,[39a] $p$-ClC$_6$H$_4$NO$_2$,[40] and 2,6-(NO$_2$)$_2$C$_6$H$_3$Cl.[39b] The difference in C–Cl bond lengths between $m$-ClC$_6$H$_4$NO$_2$ and chlorobenzene is statistically insignificant.

Conversely, the C–Br bonds in $o$- and $p$-BrC$_6$H$_4$NO$_2$ and 2,6-(NO$_2$)$_2$C$_6$H$_3$Br are not shortened relative to bromobenzene, but a shortening is observed for $m$-BrC$_6$H$_4$NO$_2$; these effects are the exact opposite of those characteristic of chlorobenzenes.

Benzene ring distortions, namely widening of the CC$_{NO_2}$C and CC$_X$C (X=Cl, Br) angles, are characteristic of $m$- and $p$-chloro(bromo)nitrobenzenes.

Non-planar conformations of $m$- and $p$-halonitrobenzenes observed in electron diffraction experiments arise as a result of nitro group torsional vibrations. Taking these vibrations into consideration has enabled us to determine the barrier to rotation about the C–NO$_2$ bond for the equilibrium planar molecular conformation, viz. 4–5 kcal mol$^{-1}$.[37] The barriers in $m$-XC$_6$H$_4$NO$_2$ and $o$-XC$_6$H$_4$NO$_2$ (X=Cl, Br) have been estimated using the new technique described above.[6] The potential functions found for the mono-
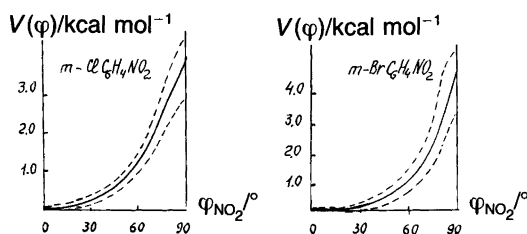
568

Fig. 4. The internal rotation potential functions for $m$-ClC$_6$H$_4$NO$_2$ and $m$-BrC$_6$H$_4$NO$_2$ (see also the legend to Fig. 3).
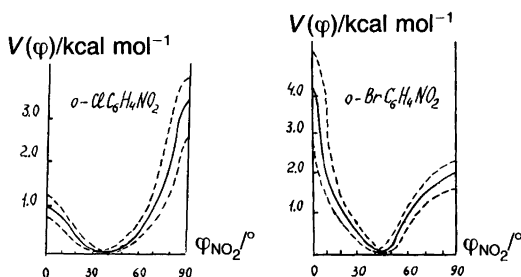


Fig. 5. The internal rotation potential functions for $o$-ClC$_6$H$_4$NO$_2$ and $o$-BrC$_6$H$_4$NO$_2$ (see also the legend to Fig. 3).

halonitrobenzenes studied are shown in Figs. 4 and 5. The functions for the $m$-nitrobenzene derivatives ClC$_6$H$_4$NO$_2$ and BrC$_6$H$_4$NO$_2$ contain broad minima in the region from 0 to 25° and maxima at 90° with the heights of the barriers to NO$_2$ group rotations being 3.7 (0.8) and 4.6 (0.9) kcal mol$^{-1}$, respectively (Fig. 4).

The following conclusions can be drawn from an analysis of the potential functions for the sterically strained $o$-halonitrobenzenes $o$-BrC$_6$H$_4$NO$_2$ and $o$-ClC$_6$H$_4$NO$_2$ (Fig. 5):

(a) the potential functions have a different form from those of $m$-derivatives;

(b) the $V(\varphi)$ curves contain narrow minima at $\varphi = 33°$ for $o$-ClC$_6$H$_4$NO$_2$ and 43° for $o$-BrC$_6$H$_4$NO$_2$, which correspond to the $\varphi$ angle values obtained by the least-squares intensity data calculations;

(c) two maxima at 0° and 90° differ in their heights: $V(90°) > V(0°)$ for $o$-ClC$_6$H$_4$NO$_2$ and $V(90°) < V(0°)$ for BrC$_6$H$_4$NO$_2$. $V(0°) = 1.0 (0.3)$ kcal mol$^{-1}$ and $V(90°) = 3.6 (0.8)$

kcal mol$^{-1}$ for $o$-ClC$_6$H$_4$NO$_2$; $V(0°) = 4.3 (1.0)$ kcal mol$^{-1}$ and $V(90°) = 2.0 (0.6)$ kcal mol$^{-1}$ for $o$-BrC$_6$H$_4$NO$_2$.

## Amplitudes of vibration

In the middle 1970's, Mastryukov and Cyvin published a series of works[42-45] whose purpose was to determine empirical relations for estimating amplitudes of vibration in organic compounds. They found that in most molecules (about 80%), the vibrational amplitudes for the CC and CH atomic pairs are related to the corresponding internuclear distances, $r$:

$$l(CC) = 0.01384 + 0.02340\,r - 0.0015\,r^2$$

$$l(CH) = 0.05014 + 0.02737\,r - 0.00180\,r^2$$

Since then, these empirical equations, which are exceedingly simple, have been employed in electron diffraction structure analyses to determine starting approximations to vibrational amplitude values. These equations, however, ignore specific features of vibrational motions in a given system. On the other hand, the development of effective programmes for calculating vibrational amplitudes[46] has limited the practical usefulness of empirical relations, which are, however, concise representations of a wealth of experimental data on a large variety of molecules.

## References

1. Cyvin, B. N., Cyvin, S. J., Vilkov, L. V. and Mastryukov, V. S. *Rev. Chim. Miner. 8* (1971) 877.
2. Sadova, N. I., Vilkov, L. V., Hargittai, I. and Brunvoll, J. *J. Mol. Struct. 31* (1976) 131.
3. Wagner, R. S. and Dailey, B. P. *J. Chem. Phys. 26* (1957) 1588.
4. Wagner, R. S., Dailey, B. P. and Solimene, N. *J. Chem. Phys. 26* (1957) 1593.
5. Chattopadnyay, S. *Indian J. Phys. 41* (1967) 759.
6. Syschikov, Yu. N., Batyukhnova, O. G., Vilkov, L. V. and Yagola, A. G. In: *Issledovanie Struktury i Energetiki Molekul* (in Russian), Ivanovo, USSR 1986, p. 64.
7. Abraham, R. J., Hearmon, R. A., Trætteberg, M. and Bakken, P. *J. Mol. Struct. 57* (1979) 149.
8. Scharfenberg, P. *J. Chem. Phys. 77* (1982) 4791.
9. Schaefer, T., Sebastian, R. and Penner, G. H. *Can. J. Chem. 64* (1986) 1372.
10. Almenningen, A., Bastiansen, O. and Trætteberg, M. *Acta Chem. Scand. 12* (1958) 1221.

11. Kuchitsu, K., Fukuyama, T. and Morino, Y. *J. Mol. Struct. 1* (1968) 463.
12. Almenningen, A. and Bastiansen, O. *Kgl. Nor. Vidensk. Selsk. Skr. 4* (1958).
13. Bastiansen, O. *Acta Chem. Scand. 4* (1950) 926.
14. Vilkov, L. V. and Sadova, N. I. *Trudy Konferentsii po Problemam Primeneniya Korrelatsionnykh Uravnenii v Organich. Khimii* (in Russian), Tartu, USSR 1962, Vol. 1, p. 240.
15. Vilkov, L. V. and Sadova, N. I. *Zh. Strukt. Khim. 8* (1967) 398.
16. (a) Akishin, P. A., Vilkov, L. V. and Mochalova, N. I. *Zh. Strukt. Khim. 2* (1961) 545; (b) Nipan, M. E., Sadova, N. I., Golubinskii, A. V. and Vilkov, L. V. *Ibid. 27* (1986) 47.
17. (a) Nipan, M. E. *Ph. D. Thesis* (in Russian), Moscow State University, Moscow 1982; (b) Skancke, P. N. *J. Comput. Chem. 4* (1983) 142.
18. Trætteberg, M., Paulen, G., Cyvin, S. J., Panchenko, Yu. N. and Mochalov, V. I. *J. Mol. Struct. 116* (1984) 141.
19. Almenningen, A., Bastiansen, O. and Skancke, P. N. *Acta Chem. Scand. 15* (1961) 711.
20. Almenningen, A., Bastiansen, O. and Walloe, L. *Selected Topics in Structure Chemistry*, Universitetsforlaget, Oslo 1967, p. 91.
21. (a) Vilkov, L. V., Mastryukov, V. S., Oppenheim, V. D. and Tarasenko, N. A. In: Cyvin, S. J., Ed., *Molecular Structures and Vibrations*, Elsevier, Amsterdam 1972, p. 310; (b) Mastryukov, V. S., Dorofeeva, O. V., Vilkov, L. V., Cyvin, B. N. and Cyvin, S. J. *Zh. Strukt. Khim. 16* (1975) 473.
22. Cyvin, B. N., Cyvin, S. J., Strelkov, S. A., Mastryukov, V. S., Vilkov, L. V. and Golubinskii, A. V. *J. Mol. Struct. 144* (1986) 385.
23. Mastryukov, V. S., Osina, E. L. and Vilkov, L. V. *Zh. Strukt. Khim. 16* (1975) 850.
24. Nahlovská, Z., Nahlovský, B. and Seip, H. M. *Acta Chem. Scand. 23* (1969) 3534.
25. Seip, H. M. *J. Chem. Phys. 54* (1971) 440.
26. Mastryukov, V. S., Golubinskii, A. V., Atatin, E. G., Vilkov, L. V., Cyvin, B. N. and Cyvin, S. J. *Zh. Strukt. Khim. 20* (1979) 726.
27. Mastryukov, V. S., Tarasenko, N. A., Vilkov, L. V., Finkelstein, E. S., Jonvik, T., Anderson, B. and Aanensen, E. *Zh. Strukt. Khim. 22* (1981) 57.
28. Almenningen, A., Dorofeeva, O. V., Mastryukov, V. S. and Vilkov, L. V. *Acta Chem. Scand., Ser. A 30* (1976) 307.
29. Dorofeeva, O. V., Mastryukov, V. S., Golubinskii, A. V., Vilkov, L. V. and Almenningen, A. *Zh. Strukt. Khim. 22* (1981) 51.
30. Dorofeeva, O. V., K Jonvik, T. and Mastryukov, V. S. *Abstracts of the Ninth Austin Symposium on Molecular Structure*, Austin, Texas 1982, p. 102.
31. Dorofeeva, O. V., Mastryukov, V. S., Allinger, N. L. and Almenningen, A. *J. Phys. Chem. 89* (1985) 252.
32. Mastryukov, V. S., Osina, E. L., Vilkov, L. V. and Hilderbrand, R. L. *J. Am. Chem. Soc. 99* (1977) 6855.
33. Skancke, P. N. *J. Mol. Struct. (Theochem.) 86* (1982) 255.
34. Trætteberg, M., Bakken, P., Seip, H. M. and Whittaker, D. *J. Mol. Struct. 116* (1984) 119.
35. Anet, F. A. L. and Krane, J. *Isr. J. Chem. 20* (1980) 72.
36. Almenningen, A., Brunvoll, J., Samdal, S., Popik, M. V., Sokolkov, S. V. and Vilkov, L. V. *J. Mol. Struct. 127* (1985) 85.
37. Almenningen, A., Brunvoll, J., Samdal, S., Popik, M. V. and Vilkov, L. V. *J. Mol. Struct. 118* (1984) 37.
38. (a) Batyukhnova, O. G., Sadova, N. I., Vilkov, L. V. and Pankrushev, Yu. A. *J. Mol. Struct. 97* (1983) 153; (b) Batyukhnova, O. G., Sadova, N. I., Syschikov, Yu. N., Vilkov, L. V. and Pankrushev, Yu. A. *Zh. Strukt. Khim. In press.*
39. (a) Batyukhnova, O. G., Sadova, N. I., Vilkov, L. V. and Pankrushev, Yu. A. *Zh. Strukt. Khim. 26* (1985) 175; (b) Batyukhnova, O. G., Vilkov, L. V., Sadova, N. I. and Pankrushev, Yu. A. *Zh. Strukt. Khim. 25* (1984) 166.
40. Sadova, N. I., Penionzhkevich, N. P. and Vilkov, L. V. *Zh. Strukt. Khim. 17* (1976) 753.
41. Penionzhkevich, N. P., Sadova, N. I. and Vilkov, L. V. *Zh. Strukt. Khim. 20* (1979) 527.
42. Mastryukov, V. S. and Cyvin, S. J. *J. Mol. Struct. 29* (1975) 15; *30* (1976) 333.
43. Osina, E. L., Mastryukov, V. S., Vilkov, L. V. and Cyvin, S. J. *Zh. Strukt. Khim. 16* (1975) 1065.
44. Mastryukov, V. S., Osina, E. L., Vilkov, L. V. and Cyvin, S. J. *Zh. Strukt. Khim. 17* (1976) 80.
45. Cyvin, S. J., Brunvoll, J., Cyvin, B. N. and Mastryukov, V. S. *Z. Naturforsch. 34 A* (1979) 1512.
46. Stølevik, R., Seip, H. M. and Cyvin, S. J. *Chem. Phys. Lett. 15* (1972) 26.