# Electron Diffraction Study of Gaseous $CH(NO_2)_3$ and $CCl(NO_2)_3$

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*Summary* The average geometrical structures of $CH(NO_2)_3$ and $CCl(NO_2)_3$ are consistent with $C_3$ models having similar parameters for C–N, N=O, and ONO, and different ones for ∠ NCN; the C–Cl bond length for the tetrahedral carbon atom in $CCl(NO_2)_3$ (1·712 Å) is the shortest yet found.

COMPARISON of the recent data for $CH_3NO_2$[1] and $CH_2ClNO_2$[2] with those for $Cl_3C—NO_2$[3] has shown that the C–N bond length increases with the number of halogen atoms (see Table). We have now studied the influence of the number of nitro-groups on the structure of $CH(NO_2)_3$ and $CCl(NO_2)_3$.

Our electron diffraction patterns were obtained on a reconstructed commercial apparatus EG-100A ($r^3$ sector) with a sample temperature of 70 °C for $CH(NO_2)_3$ and 45 °C for $CCl(NO_2)_3$. The merged $sM(s)$ curves from two camera distances were in the range $3{\cdot}4 < s < 31{\cdot}0$ Å$^{-1}$ for $CH(NO_2)_3$ and $4{\cdot}8 < s < 34{\cdot}2$ Å$^{-1}$ for $CCl(NO_2)_3$.

Preliminary determination of geometrical parameters was based on the radial distribution curve after assuming $C_3$ symmetry for both molecules and planarity of the $CNO_2$-groups. Further refinement was carried out by least-squares analysis of the $sM(s)$ curves by the program due to Seip.[4]

The final results are listed in the Table. The $R$-factors, $[\Sigma w_\Delta^2/\Sigma w|sM(s)|^2]^{\frac{1}{2}}$ were 8·3 and 7·9% respectively.

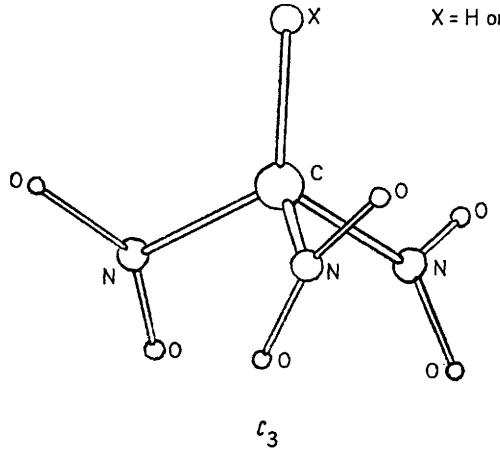


FIGURE. Model of the $CX(NO_2)_3$ molecule.

The main parameters (see Table) are similar for $CH(NO_2)_3$, $CCl(NO_2)_3$, $CH_3NO_2$, and $CH_2ClNO_2$, but are different in

TABLE. Structural parameters for the nitro-compounds.

| Parameters | $CH_3NO_2$[1] | $CH_3NO_2$[7] | $ClCH_2NO_2$[2] | $CCl_3NO_2$[3] | $CH(NO_2)_3$[a] (present work) | $CCl(NO_2)_3$ (present work) |
|---|---|---|---|---|---|---|
| $r$(C–H) Å | 1·088(ass.) | 1·080(9) | — | 1·095(ass.) | 1·13(ass.) | — |
| $r$(C–Cl) Å | — | — | 1·765 (9) | 1·726 (5) | — | 1·712(4) |
| $r$(N=O) Å | 1·224(5) | 1·225(1) | 1·230(2) | 1·190(6) | 1·219(2) | 1·213(1) |
| $r$(C–N) Å | 1·489(5) | 1·499(2) | 1·493(10) | 1·594(20) | 1·505(5) | 1·513(3) |
| ∠ HCN | 107·2(0·5) | 109·0(3·0) | 111(ass.) | — | 108·6(0·6) | — |
| ∠ ClCN | — | — | 114(1) | 106·0(1,1) | — | 112·1(0·5) |
| ∠ ONO | 125·3(0·5) | 125·0(0·2) | 128(2) | 131·7(2·6) | 128·6(0·3) | 128·3(0·5) |

[a] Mean amplitudes for $HC(NO_2)_3$ are $l$(C–N) 0·049(2), $l$(N=O) 0·052(2), and those for $CCl(NO_2)_3$ are $l$(C–Cl) 0·037(5), $l$(C–N) 0·051(3), $l$(N=O) 0·040(1). Standard deviations from least-squares analyses are given in parentheses. The scale factor does not exceed 0·1%. These do not include estimates of systematic error.

$CCl_3NO_2$, especially the C–N bond length. The C–Cl bond lengths are similar, being shortest in $CCl_3NO_2$ and $CCl(NO_2)_3$. The C–Cl bond length in the latter is even shorter than in $CH_2$=$CHCl$[5] (1·728 Å). Thus the tetrahedral C–Cl bond length varies within an interval of *ca.* 0·1 Å, from 1·71 Å in $CCl(NO_2)_3$ to 1·828 Å in $CCl(CH_3)_3$.

The average conformation for each molecule corresponds to $NO_2$ torsion angles of 26° for $CH(NO_2)_3$ and 49° for $CCl(NO_2)_3$. The $NO_2$ torsion angle $\phi$ is 0° for the conformation in which the bonds C–X (X = H or Cl) and N=O lie in the same plane.

The vibration amplitudes for the pairs of atoms N···O and O···O, depending on the torsion, are very large (0·17—0·20 Å), confirming that the barrier to internal rotation for $\phi = 0°$ is small.

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