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Freezing conformation of polychloronitrophenyl *N*-substituted morpholines studied by DNMR and X-ray crystal structure

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The acceleration of SNAr reaction of aromatic halides has been studied with various amines under high pressure. Compounds having high steric hindrance as 2-morpholino-substituted polychloro-1-nitrobenzenes were obtained. These showed different behaviours of methylene protons of morphlino ring at room temperature apparently related to the higher steric hindrance. So these compounds were investigated using dynamic ^{1}H NMR and single crystal X-ray crystallography.

Keywords: conformation of polychloronitrophenyl *N*-substituted morpholines

The authors have obtained a series of title compounds by high pressure reactions.[1] Measurement of ^{1}H NMR spectra of these compounds at room temperature showed the interesting behaviour of the methylene protons of the morpholino ring. The ^{1}H NMR spectrum of 2-morpholino-3,4,5,6-tetrachloro-1-nitrobenzene **1** shows broadening of signals from the protons on the ring below about 58 °C, (2-morpholino-3,5,6-trichloro-1-nitrobenzene **2**, 48 °C) and eventually splitting into multiplets of an AA′BB′ spin system below 0 °C (**2**, –10 °C), but the signals gave no change on further cooling to –90 °C. A line shape matching of experimental and calculated spectra yields the barriers $\Delta G^{\neq}$ of **1** and **2** as 15.8 and 15.0 kcal/mol. The barriers for 2-morpholino-4,6-dichloro-1-nitrobenzene **3** and morpholine **4** are 7.7 and 10.3 kcal/mol. The thermal behaviour of this system may usually relate with the three possible processes, namely N–CAr bond rotation, ring inversion and nitrogen inversion. The nitrogen and ring inversion barriers are expected to be about 6 and 10 kcal/mol.[3,4] So it is reasonable to conclude that the barriers measured for **1**, **2** and **3** are due to N–CAr bond rotation. Because of the bulkiness of a nitro group, rotation of **3** is faster at a given temperature for a lower barrier (7.7 kcal/mol). However, the morpholino ring of **2** is placed between the nitro group and the chlorine atom like a sandwich and so has a large rotation barrier and the ring is frozen. The rotation barrier of **1** is increased 0.8 kcal/mol by an additional *meta*-chlorine atom.

The results of an X-ray diffraction study supported this conclusion. Compound **2** in the solid state has a very big steric hindrance leading to the plane through C6, C7, C8 and C9 of the morpholino group being almost perpendicular to the benzene ring with dihedral angle of 89.45° and the nitro group of 92.3°, respectively.

Crystal data for **2** –$C_{10}H_9N_2O_3Cl_3$; Mr = 311. 55, monoclinic: a = 17.515(2), b = 7.8246(5), c = 9.5859(5) Å,β = 98.48(1)°, V=1229.3Å^3, space group $P2_1/a$, Z = 4, dx = 1.59g cm^{-3}, μ(Cu·Kα), = 65.7 cm^{-3}. The experimental data were collected on a Rigaku four-circle diffractometer, model AFC-5, with Ni-filtered Cu·Kα (λ = 1.54184 Å) radiation. The structure was solved by direct methods (SHELXS-86), and refined by block-diagonal least-squares techniques. The final R value was 4.1%.

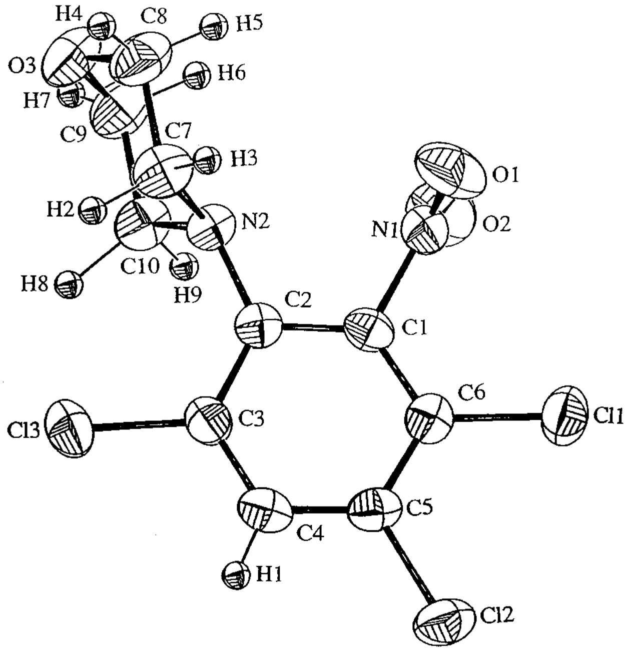

Fig. 4 ORTEP drawing of **2** with atomic numbering scheme.

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