X-Ray Investigation of p-Nitroanisole

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The following is an account of an X-ray structural study of p-nitroanisole based on diffraction data collected at −165 °C. The measurements were done using a SYNTEX P1 diffractometer and a prismatic crystal of dimensions 0.3 × 0.3 × 0.1 mm. Apart from the following details, data relevant to data collection and data treatment may be found in publications devoted to X-ray investigations of C-nitroso compounds performed in this laboratory.1 Within a quadrant of reciprocal space and with 2θ_{max} = 65° (MoKα radiation) 1427 reflections were measured; 759 had intensities larger than 2.5σ(I) and were used in the further work. The scan limits were 2θ(x₁) = 1.1° and 2θ(x₂) = 1.3°. Atomic scattering factors and computer programs used are referred to in the publications mentioned.1 The crystal data for p-nitroanisole at −165 °C are:

C₇H₈O₂N, monoclinic, space group P2₁/c, a = 9.045(3) Å, b = 10.573(6) Å, c = 7.533(2) Å, β = 100.56(2)°, V = 708.2 Å³, M = 153.14, D_{calc} = 1.436 g cm⁻³, Z = 4, F(000) = 320. The structure was determined by use of the MULTAN program package. Isotropic least-squares full matrix refinement yielded a conventional R factor of 17.4%. The improvement achieved by introducing anisotropy was unusually large, R dropping to 8.8%. At this stage all hydrogen atoms could be located in a subsequently calculated ΔF map. The refinement converged to R = 0.048, a weighted R_w of 0.042 and a goodness of fit S of 1.8. Final parameters are given in Table 1. The estimated standard deviations are from 0.003 to 0.006 Å in bond lengths and 0.4–0.5° in angles involving only non-hydrogen atoms. The C–H bond lengths are in the range 0.87–1.10 Å with e.s.d.'s of 0.03–0.04 Å. Other structural results are given in Fig. 1. In this the view is down the normal to planes containing edge-to-edge and head-to-tail packed molecules. Some interlayer contacts are: O41···O41': 3.049 Å, N4···O1: 3.244 Å and C2···C5: 3.429 Å. Both the benzene ring with O1 and N4 and the CNO₂ group are planar. The corresponding interplanar angle is 7.3° while the torsion about the C–OMe bond is 59.6°. The title compound resembles p-nitrophenol closely as to the bond lengths, especially in the nitro group, considering the x-form of the phenol.2 For all the corresponding bond lengths ΔR_{rms} = 0.011 Å. The only significant difference is in the C5–C6 distance. This is gratifying in view of the identical IR-KBr-ω_NO

Fig. 1. A stereoscopic illustration of the structure including numbering of atoms and bond lengths (Å) and angles (°). The ellipsoids are those of 50% probability.

Table 1. Fractional atomic coordinates and thermal parameters. The anisotropic temperature factors are expressed as: \( \text{exp}[-2\pi^2(h^2a^2U_{11} + \cdots + 2kh*c*U_{23})] \). Estimated standard deviations in parentheses.

![Chemical Figure]

Fig. 2. A plot of the N–O bond length (\( R_{NO} \)) against the C–N bond length (\( R_{CN} \)) in the compounds potassium \( \alpha \)-nitrophenolate hemihydrate (A), \( \beta \)-nitrophenol \( \alpha \) form (B), \( \beta \)-nitroanisole (C), 4-nitropyridine N-oxide (D), 4-nitrobenzidiazoc-4'-methoxythiophenolate (E), \( p \)-nitrodiphenyl (F), 2-p-nitroacetophenone (G), \( \alpha \)-chloro-4-nitrobenzaldehyde (H), 2,3-dimethyl-4-nitropyridine N-oxide tetragonal form (I), \( p \)-dimethylaminobenzylidenep-nitroaniline (J), 2-p-nitrobenzaldoxime (K), \( p \)-methylbenzylidenep-nitroanil (L), 4-nitro-\( N \)-methylbenzaldehyde (M), \( m \)-nitrophenol (N), \( \beta \)-nitrobenzoxol[3-phenyl-2-1 pentene-4-one (O), \( p \)-nitrobenzidiazoc-4'-nitrobenzoic acid (Q), and 2,4-dinitrophenol (R). Vertical bars show \( \Delta R_{NO} \) while horizontal bars indicate the e.s.d. in \( R_{CN} \). The least-squares lines shown is for the (bullet) points (low temperature or librational correction).


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