

X-Ray Investigation of *p*-Nitroanisole

H. J. TALBERG

Department of Chemistry, University of Oslo
Oslo 3, Norway

The following is an account of an X-ray structural study of *p*-nitroanisole based on diffraction data collected at $-165\text{ }^{\circ}\text{C}$. The measurements were done using a SYNTEX P1 diffractometer and a prismatic crystal of dimensions $0.3 \times 0.3 \times 0.1\text{ mm}$. 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 $2\theta_{\text{max}} = 65^{\circ}$ (MoK α radiation) 1427 reflections were measured; 759 had intensities larger than $2.5\sigma(I)$ and were used in the further work. The scan limits were $2\theta(\alpha_1) - 1.1^{\circ}$ and $2\theta(\alpha_2) + 1.3^{\circ}$. Atomic scattering factors and computer programs used are referred to in the publications mentioned.¹ The crystal data for *p*-nitroanisole at $-165\text{ }^{\circ}\text{C}$ are: $\text{C}_7\text{H}_7\text{O}_3\text{N}$, monoclinic, space group $P2_1/c$, $a = 9.045(3)\text{ \AA}$, $b = 10.573(6)\text{ \AA}$, $c = 7.533(2)\text{ \AA}$, $\beta = 100.56(2)^{\circ}$, $V = 708.2\text{ \AA}^3$, $M = 153.14$, $D_{\text{calc}} = 1.436$

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 \AA in bond lengths and $0.4\text{--}0.5^{\circ}$ in angles involving only non-hydrogen atoms. The C–H bond lengths are in the range 0.87–1.10 \AA with e.s.d.'s of 0.03–0.04 \AA . 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: $\text{O41}\cdots\text{O41}'$: 3.049 \AA , $\text{N4}\cdots\text{O1}$: 3.244 \AA and $\text{C2}\cdots\text{C5}$: 3.429 \AA . Both the benzene ring with O1 and N4 and the CNO_2 group are planar. The corresponding interplanar angle is 7.3° while the torsion about the C–Ome bond is $5.9(6)^{\circ}$. The title compound resembles *p*-nitrophenol closely as to the bond lengths, especially in the nitro group, considering the α -form of the phenol.² For all the corresponding bond lengths $\Delta R_{\text{rms}} = 0.011\text{ \AA}$. The only significant difference is in the C5–C6 distance. This is gratifying in view of the identical IR-KBr- ω_{NO}

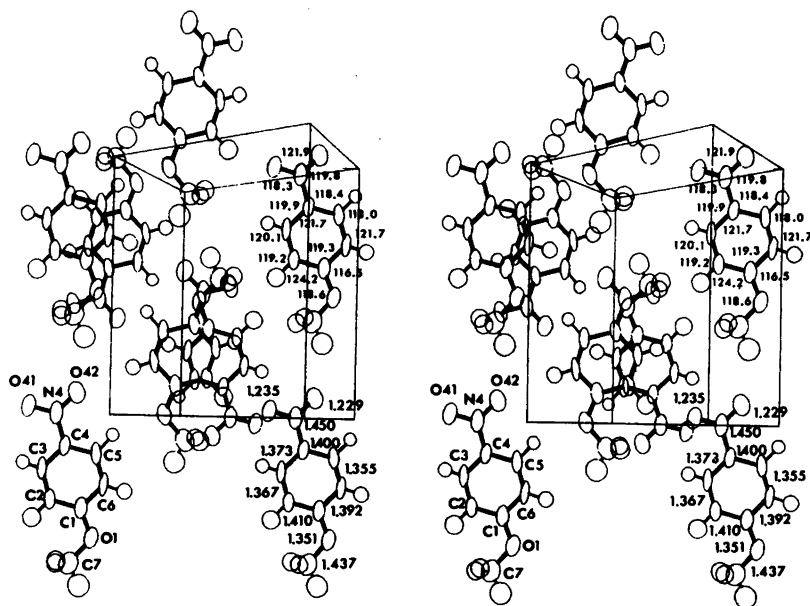


Fig. 1. A stereoscopic illustration of the structure including numbering of atoms and bond lengths (\AA) and angles ($^{\circ}$). The ellipsoids are those of 50% probability.

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

ATOM	X	Y	Z	U11	U22	U33	U12	U13	U23
O1	.14460(29)	.00071(41)	.39346(30)	.0344(14)	.0843(29)	.0433(17)	-.0113(20)	.0105(13)	-.0069(22)
O41	.41471(27)	.52755(28)	.65244(36)	.0404(16)	.0907(31)	.0363(16)	-.0090(17)	.0004(13)	-.0134(18)
O42	.22109(34)	.58449(33)	.45777(44)	.0615(20)	.0877(30)	.0542(22)	.0101(21)	.0036(17)	.0001(20)
N4	.30170(37)	.50173(47)	.53940(44)	.0319(19)	.0994(43)	.0263(18)	-.0033(26)	.0006(15)	-.0064(27)
C1	.19000(41)	.12049(53)	.43800(52)	.0265(25)	.0856(49)	.0235(25)	-.0074(25)	.0119(20)	.0004(27)
C2	.37710(41)	.15249(53)	.04064(51)	.0235(21)	.0774(42)	.0264(23)	-.0053(27)	.0047(19)	.0060(26)
C3	.36253(41)	.27723(56)	.07909(53)	.0172(28)	.0904(47)	.0217(21)	-.0078(26)	.0002(16)	.0023(28)
C4	.26406(39)	.36964(53)	.00466(49)	.0236(22)	.0762(41)	.0206(23)	-.0077(23)	.0050(18)	-.0075(23)
C5	.12683(40)	.34015(53)	.39335(54)	.0209(21)	.0950(48)	.0203(19)	.0061(27)	.0023(17)	-.0054(20)
C6	.09319(38)	.21651(52)	.36840(52)	.0102(21)	.1023(49)	.0169(21)	-.0096(27)	-.0005(16)	-.0002(29)
C7	.23302(64)	-.10100(69)	.40009(77)	.0622(34)	.0936(68)	.0497(35)	-.0145(37)	.0262(29)	-.0004(36)

ATOM	X	Y	Z	B	ATOM	X	Y	Z	B
H5	.0040(34)	.4174(29)	.3301(43)	2.6(8)	H6	.0027(30)	.1910(30)	.2816(46)	3.7(9)
H3	.4477(33)	.3004(33)	.6400(44)	3.0(9)	H2	.4051(42)	.0700(37)	.6076(60)	5.3(11)
H71	.1906(43)	-.1906(45)	.4426(59)	7.2(18)	H72	.3339(40)	-.1021(34)	.4442(49)	5.3(10)
H73	.2450(36)	-.0916(33)	.6143(54)	4.6(9)					

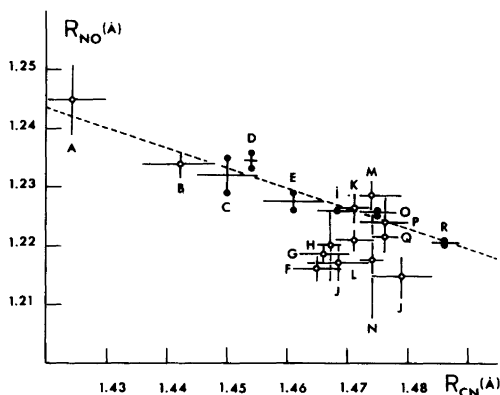


Fig. 2. A plot of the N—O bond length (R_{NO}) against the C—N bond length (R_{CN}) in the compounds potassium *o*-nitrophenolate hemihydrate (A),³ *p*-nitrophenol α form (B),² *p*-nitroanisole (C), 4-nitropyridine *N*-oxide (D),² 4(nitrobenzidiazolo-4'-methoxythiophenolate (E),⁴ *p*-nitrodiphenyl (F),² *p*-nitroacetophenone (G),² α -chloro-4-nitrobenzaldoxime (H),² 3,5-dimethyl-4-nitropyridine *N*-oxide tetragonal form (i),⁵ *p*-dimethylaminobenzylidene-*p*-nitroaniline (J),² *p*-nitrobenzaldoxime (K),² *p*-methylbenzylidene-*p*-nitroaniline (L),² 4-nitro-*N*-methylbenzaldoxime (M),² *m*-nitrophenol (N),² 2-(*p*-nitrobenzoyloxy)-3-phenyl-2-pentene-4-one (O),⁶ *p*-nitrobenzylidene-*p*-dimethylaminoaniline (P),² *p*-nitrobenzoic acid (Q),⁷ and 2,4-dinitrophenol (R).⁸ Vertical bars show ΔR_{NO} while horizontal bars indicate the e.s.d. in R_{CN} . The least-squares line shown is for the ●-points (low temperature or librational correction).

wavenumbers for the two compounds. The title compound is compared with some recently studied nitrobenzenes and pyridines in an R_{NO}/R_{CN} plot in Fig. 2 (X-ray, complete data sets). It appears that the point for this investigation (C) lies close to a correlation line established by points being weakly influenced by thermal vibration effects (B, C, D and O are for low temperature studies). Mutual conjugation seems to cause a 0.025 Å shortening of the C—N bond in *p*-nitroanisole. A rigid body analysis of the entire molecule shows moderate agreement between observed and calculated tensor elements: $\Delta U_{rms} = 0.0044 \text{ \AA}^2$. The r.m.s. eigenvalues of L are 4.2, 3.1 and 2.2° and those of T 0.30, 0.13 and 0.13 Å. It appears from Fig. 1, that the unusually strong translational oscillation is in the direction of the *b* axis. This anisotropy in the translational oscillation is paralleled by anisotropy in the dependency of the unit cell dimensions upon temperature: *a* and *c* decrease the usual 2–3 % while *b* is constant when lowering the temperature from 20 to –165 °C.

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