Acta Cryst. (1982). B**38**, 3119–3120

4-*tert*-Butyl-3,5-dinitroanisole

By W. Van Havere, A. T. H. Lenstra and H. J. Geise

University of Antwerp (*UIA*), *Department of Chemistry*, *Universiteitsplein* 1, *B*-2610 *Wilrijk*, *Belgium*

(*Received* 22 *April* 1982; *accepted* 18 *June* 1982)

Abstract. $C_{11}H_{14}N_2O_5$, triclinic, $P\bar{1}$, $Z = 2$, $a = 8{\cdot}887\,(3)$, $b = 10{\cdot}148\,(3)$, $c = 8{\cdot}024\,(4)$ Å, $\alpha = 110{\cdot}49\,(4)$, $\beta = 112{\cdot}15\,(5)$, $\gamma = 89{\cdot}58\,(3)^\circ$, $D_x = 1{\cdot}359$ Mg m^{-3}, μ(Mo $K\alpha$) $= 0{\cdot}117$ mm^{-1}. $R_w = 0{\cdot}029$ for 1617 observed reflections. The structure was solved by *MULTAN*. Severe crowding in the molecule causes the phenyl ring to adopt a boat conformation and the nitro groups to twist with respect to the benzene nucleus.

Introduction. Pulay, Fogarasi & Boggs (1981) calculated that the force constant to bend benzene into a boat form [f(boat) = 0·4105 aJ rad^{-1}] is smaller than the force constant to bend it into a chair form [f(chair) = 0·4894 aJ rad^{-1}]. Therefore, if severe crowding forces a phenyl ring into a non-planar conformation, the distortion would rather be towards a boat than towards a chair form.

4-*tert*-Butyl-3,5-dinitroanisole (abbreviated BNA) seemed a good candidate to reveal this. Non-planar geometries of simple aromatic rings have to our knowledge only been reported for pyridine derivatives (Lenstra & Petit, 1980; Van Havere, Lenstra, Geise, Van den Berg & Benschop, 1982).

2703 independent reflection intensities up to $\theta = 27^\circ$ were collected at room temperature on an Enraf–Nonius CAD-4 diffractometer using Zr-filtered Mo radiation. A pure ω scan was employed. 1617 reflections for which $I > 2\sigma(I)$ were used in the analysis. The low absorption coefficient ($\mu = 0{\cdot}117$ mm^{-1}) and the small size of the crystal (0·3 × 0·3 × 0·2 mm) made correction for absorption unnecessary. The structure was solved by *MULTAN* (Germain, Main & Woolfson, 1971); the most likely E map with 200 terms showed all the non-hydrogen atoms.

A subsequent difference electron density map revealed the positions of all H atoms. In the least-squares refinement with the Gauss–Seidel block method (Sparks, 1974) and the Enraf–Nonius *SDP* package (Frenz, 1978) each reflection was given a weight based on counting statistics. Debye–Waller temperature parameters of H atoms were fixed at 3·0 Å^2 for H atoms bound to the aromatic ring and at 5·0 Å^2 for the others. The isotropic extinction parameter (Zachariasen, 1963) was refined to $r = 0{\cdot}29 \times 10^{-6}$ mm; the R_w value converged to 0·029 with $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$. The maximum noise level in the final difference Fourier map was 0·14 e Å^{-3}.

Table 1. *Positional parameters in fractions of cell edges with e.s.d.'s in parentheses*

Isotropic temperature factors (Å^2) of non-hydrogen atoms are calculated from the anisotropic temperature parameters assuming equal volume of the 50% probability region; $B_{\rm iso}$ [$= 8\pi^2 \times (U^0_{11}U^0_{22}U^0_{33})^{1/3}$ was calculated according to Lipson & Cochran (1966). All anisotropic thermal parameters were physically acceptable. H(j,x) with j = 1, 2, 3 is attached to atom x.

	x	y	z	$B_{\rm iso}$
O(1)	0·3689 (2)	1·0003 (2)	0·3228 (2)	6·54
O(2)	0·1674 (1)	0·8269 (2)	0·1620 (2)	6·05
O(3)	0·4569 (2)	0·6561 (1)	−0·4943 (2)	6·12
O(4)	0·2324 (2)	0·5493 (2)	−0·5257 (2)	6·50
O(5)	0·7465 (1)	0·6400 (1)	0·1862 (2)	5·41
N(1)	0·3003 (2)	0·8866 (2)	0·1940 (2)	4·87
N(2)	0·3624 (2)	0·6285 (1)	−0·4295 (2)	4·75
C(1)	0·6108 (2)	0·6789 (2)	0·0762 (2)	3·98
C(2)	0·5231 (2)	0·7618 (2)	0·1719 (2)	4·04
C(3)	0·3859 (2)	0·8083 (2)	0·0707 (2)	3·65
C(4)	0·3226 (2)	0·7809 (2)	−0·1289 (2)	3·45
C(5)	0·4135 (2)	0·6901 (2)	−0·2151 (2)	3·60
C(6)	0·5532 (2)	0·6409 (2)	−0·1210 (2)	3·93
C(7)	0·1799 (2)	0·8500 (2)	−0·2328 (2)	3·98
C(8)	0·1993 (2)	0·8691 (2)	−0·4060 (2)	5·34
C(9)	0·1813 (2)	1·0011 (2)	−0·0982 (2)	5·10
C(10)	0·0147 (2)	0·7608 (2)	−0·3032 (3)	5·88
C(11)	0·8457 (2)	0·5621 (2)	0·0944 (3)	6·17
H(C2)	0·557 (1)	0·788 (1)	0·304 (2)	3·50
H(C6)	0·600 (1)	0·587 (1)	−0·189 (2)	3·50
H(1,C8)	0·313 (2)	0·911 (1)	−0·370 (2)	5·00
H(2,C8)	0·171 (2)	0·785 (1)	−0·517 (2)	5·00
H(3,C8)	0·122 (2)	0·928 (1)	−0·445 (2)	5·00
H(1,C9)	0·292 (2)	1·054 (1)	−0·036 (2)	5·00
H(2,C9)	0·105 (2)	1·048 (1)	−0·175 (2)	5·00
H(3,C9)	0·145 (2)	1·004 (1)	0·004 (2)	5·00
H(1,C10)	0·012 (2)	0·666 (1)	−0·390 (2)	5·00
H(2,C10)	−0·001 (2)	0·751 (1)	−0·193 (2)	5·00
H(3,C10)	−0·069 (2)	0·806 (1)	−0·363 (2)	5·00
H(1,C11)	0·875 (2)	0·612 (1)	0·030 (2)	5·00
H(2,C11)	0·785 (2)	0·478 (1)	−0·012 (2)	5·00
H(3,C11)	0·932 (2)	0·549 (1)	0·198 (2)	5·00

0567-7408/82/123119-02$01.00

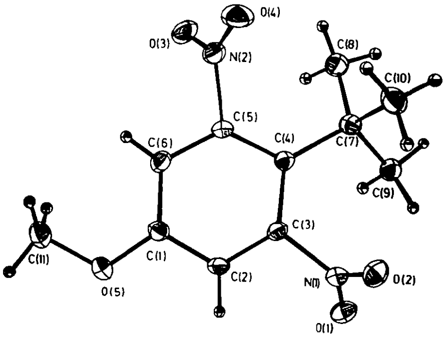

Fig. 1. Numbering of atoms and conformation.

Refined parameters are listed* in Table 1, the numbering of the atoms is given in Fig. 1.

Discussion. Bond lengths, valence angles and a selection of torsion angles are given in Tables 2, 3 and 4, respectively.

The crowding, notably at C(3), C(4) and C(5), is reflected in a slight lengthening of C(3)–C(4), C(4)–C(5) and C(4)–C(7) as well as in abnormal values for the valence angles at the above-mentioned centres. Relief of steric strain is also achieved by rotating both NO_2 groups over a large angle (63 and 67°) with respect to the aromatic ring. Despite this, the sum of the valence angles around each of the atoms C(3), C(4), C(5), N(1) and N(2) remains 360°.

Table 2. *Bond lengths* (Å) *with e.s.d.'s in parentheses*

C(1)–C(2)	1·376 (2)	C(1)–C(6)	1·371 (2)
C(2)–C(3)	1·372 (2)	C(5)–C(6)	1·382 (2)
C(3)–C(4)	1·404 (2)	C(4)–C(5)	1·394 (2)
C(1)–O(5)	1·351 (1)	C(7)–C(8)	1·539 (2)
O(5)–C(11)	1·420 (2)	C(7)–C(9)	1·533 (2)
C(4)–C(7)	1·547 (2)	C(7)–C(10)	1·526 (2)
C(3)–N(1)	1·482 (2)	C(5)–N(2)	1·490 (1)
N(1)–O(1)	1·213 (1)	N(2)–O(3)	1·220 (1)
N(1)–O(2)	1·225 (1)	N(2)–O(4)	1·218 (1)

Table 3. *Valence angles* (°) *with e.s.d.'s in parentheses*

C(2)–C(1)–C(6)	118·1 (1)	C(3)–C(4)–C(5)	110·0 (1)
C(1)–C(2)–C(3)	119·9 (1)	C(1)–C(6)–C(5)	119·3 (1)
C(2)–C(3)–C(4)	126·1 (1)	C(4)–C(5)–C(6)	126·5 (1)
C(2)–C(1)–O(5)	116·5 (1)	C(3)–C(4)–C(7)	124·3 (1)
C(6)–C(1)–O(5)	125·4 (1)	C(5)–C(4)–C(7)	125·6 (1)
C(1)–O(5)–C(11)	118·0 (1)		
C(4)–C(7)–C(8)	111·3 (1)	C(8)–C(7)–C(9)	104·5 (1)
C(4)–C(7)–C(9)	111·0 (1)	C(8)–C(7)–C(10)	109·4 (1)
C(4)–C(7)–C(10)	110·9 (1)	C(9)–C(7)–C(10)	109·6 (1)
C(2)–C(3)–N(1)	112·4 (1)	C(6)–C(5)–N(2)	111·5 (1)
C(4)–C(3)–N(1)	121·5 (1)	C(4)–C(5)–N(2)	122·0 (1)
C(3)–N(1)–O(1)	118·4 (1)	C(5)–N(2)–O(3)	117·7 (1)
C(3)–N(1)–O(2)	116·4 (1)	C(5)–N(2)–O(4)	117·2 (1)
O(1)–N(1)–O(2)	125·1 (1)	O(3)–N(2)–O(4)	125·1 (1)

Table 4. *Selection of torsion angles* (°) (*e.s.d.'s are about* 0·3°)

O(1)–N(1)–C(3)–C(2)	67·1	O(3)–N(2)–C(5)–C(6)	–62·7
O(2)–N(1)–C(3)–C(2)	–109·8	O(4)–N(2)–C(5)–C(6)	114·1
O(2)–N(1)–C(3)–C(4)	66·8	O(4)–N(2)–C(5)–C(4)	–63·3
O(1)–N(1)–C(3)–C(4)	–116·3	O(3)–N(2)–C(5)–C(4)	119·8
C(8)–C(7)–C(4)–C(5)	–27·6	C(10)–C(7)–C(4)–C(3)	–89·6
C(9)–C(7)–C(4)–C(3)	32·5	C(10)–C(7)–C(4)–C(5)	94·5
C(11)–O(5)–C(1)–C(6)	5·0		
C(3)–C(2)–C(1)–C(6)	–2·4	C(2)–C(1)–C(6)–C(5)	1·9
C(1)–C(6)–C(5)–C(4)	2·0	C(6)–C(5)–C(4)–C(3)	–4·7
C(5)–C(4)–C(3)–C(2)	4·1	C(4)–C(3)–C(2)–C(1)	–0·8

However, the most remarkable response of the molecule to the steric crowding is a small, but significant, deviation from planarity of the benzene nucleus itself.

Inspection of the relevant torsion angles (Table 4) reveals that the conformation tends towards a true boat with C(1) and C(4) as bowsprits. This conclusion also follows from the Cremer & Pople (1975) coordinates: $q_2 = 0{\cdot}042$ (1), $q_3 = -0{\cdot}010$ (1), $Q = 0{\cdot}043$ (1) Å, $\varphi_2 = 7$ (2)° and $\theta_2 = 104$ (2)°.

Excluding the OCH_3 substituent, but including the H atoms of the *tert*-butyl group, the molecule possesses C_s symmetry in the solid state. This and the consideration that all the geometrical features of BNA are caused by intramolecular forces alone is a strong indication that the molecule has essentially the same geometry in solution as in the crystal.

References

Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.

Frenz, B. A. (1978). *The Enraf-Nonius CAD-4 – SDP. Computing in Crystallography*, edited by H. Schenk, R. Olthof-Hazekamp, H. van Koningsveld & G. C. Bassi, pp. 64–71. Delft Univ. Press.

Germain, G., Main, P. & Woolfson, M. M. (1971). *Acta Cryst.* A**27**, 368–376.

Lenstra, A. T. H. & Petit, G. H. (1980). *Cryst. Struct. Commun.* **9**, 725–730.

Lipson, H. & Cochran, W. (1966). *The Determination of Crystal Structures*, pp. 300 ff. London: Bell.

Pulay, P., Fogarasi, G. & Boggs, J. E. (1981). *J. Chem. Phys.* **74**, 3999–4014.

Sparks, R. A. (1974). Least-squares tutorial, Proc. Am. Crystallogr. Assoc. Meeting, Berkeley, California, pp. 99 ff.

Van Havere, W., Lenstra, A. T. H., Geise, H. J., Van den Berg, G. R. & Benschop, H. P. (1982). *Acta Cryst.* B**38**, 1635–1637.

Zachariasen, W. H. (1963). *Acta Cryst.* **16**, 1139–1144.

---

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38021 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.