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References

Abad-Zapatero, C., Abdel-Mequid, S. S., Johnson, J. E., Leslie, A. G. W., Rayment, I., Rossmann, M. G., Suck, D. & Tsukihara, T. (1980). *Nature (London)*, **286**, 33–39.

Acharya, R., Fry, E., Stuart, D., Fox, G., Rowlands, D. & Brown, F. (1989). *Nature (London)*, **337**, 709–716.

Arnond, E., Vriend, G., Luo, M., Griffith, J. P., Kamer, G., Erickson, J. W., Johnson, J. E. & Rossmann, M. G. (1987). *Acta Cryst.* A**43**, 346–361.

Bernal, J. D. & Carlisle, C. H. (1948). *Nature (London)*, **162**, 139–140.

Bernstein, F. C., Koetzle, T. F., Williams, G. J. B., Meyer, E. F., Brice, M. D., Rogers, J. R., Kennard, O., Shimanouchi, T. & Tasumi, M. J. (1977). *J. Mol. Biol.* **112**, 535–542.

Bol, J. F., Kraal, B. & Brederode, F. Th. (1974). *Virology*, **58**, 101–110.

Chidlow, J. & Tremaine, J. H. (1971). *Virology*, **43**, 267–278.

Cohen, S. S. & Greenberg, M. L. (1981). *Proc. Natl Acad. Sci. USA*, **78**, 5470–5474.

Colman, P. M., Tulloch, P. A., Shukla, D. D. & Gough, K. H. (1980). *J. Mol. Biol.* **142**, 263–268.

Cuillel, M., Jacrot, M. & Zulauf, M. (1981). *Virology*, **110**, 63–72.

Dupin, A., Peter, R., Collot, D., Das, B. C., Peter, C., Bouillon, P. & Duranton, H. (1984). *C. R. Acad. Sci. Sér. C*, **298**, 219–221.

Durham, A. C. H., Witz, J. & Bancroft, J. B. (1984). *Virology*, **133**, 1–8.

Heuss, K. L., Mohana Rao, J. K. & Argos, P. (1981). *J. Mol. Biol.* **146**, 629–633.

Jacrot, B., Chauvin, C. & Witz, B. (1977). *Nature (London)*, **266**, 417–421.

Kaper, J. M. (1971). *J. Mol. Biol.* **56**, 259–276.

Kaper, J. M. (1975). *Frontiers of Biology*, Vol. 39, edited by A. Neuberger & E. L. Tatiem, pp. 273–320. Amsterdam: North-Holland.

Katouzian-Safadi, M. & Berthet-Colominas, C. (1983). *Eur. J. Biochem.* **137**, 47–55.

Katouzian-Safadi, M., Favre, A. & Haenni, A.-L. (1980). *Eur. J. Biochem.* **112**, 478–486.

Katouzian-Safadi, M. & Haenni, A.-L. (1986). *J. Gen. Virol.* **67**, 557–565.

Keeling, J. & Matthews, R. E. F. (1982). *Virology*, **119**, 214–218.

Klug, A., Longley, W. & Lebermann, R. (1966). *J. Mol. Biol.* **15**, 315–343.

Liljas, L. (1986). *Prog. Biophys. Mol. Biol.* **48**, 1–36.

Mellema, J. E. & Amos, L. A. (1972). *J. Mol. Biol.* **72**, 819–822.

Moline, H. E. & Fries, R. E. (1974). *Phytopathology*, **64**, 44–48.

Munshi, S. K., Hiremath, C. N., Murthy, M. R. N. & Savithri, H. S. (1987). *Acta Cryst.* B**43**, 376–382.

Munshi, S. K. & Murthy, M. R. N. (1986). *J. Appl. Cryst.* **19**, 61–62.

Nixon, H. L. & Gibbs, A. J., (1960). *J. Mol. Biol.* **2**, 197–200.

Peter, R., Stehelin, D., Reinbolt, J., Collot, D. & Duranton, H. (1972). *Virology*, **49**, 615–617.

Rayment, I., Johnson, J. E., Suck, D., Akimoto, T. & Rossmann, M. G. (1978). *Acta Cryst.* B**34**, 567–578.

Rossmann, M. G. (1979). *J. Appl. Cryst.* **12**, 225–238.

Rossmann, M. G. & Blow, D. M. (1962). *Acta Cryst.* **15**, 24–31.

Rossmann, M. G., Ford, G. C., Watson, H. C. & Banaszak, L. J. (1972). *J. Mol. Biol.* **64**, 237–249.

Savithri, H. S. & Erickson, J. W. (1983). *Virology*, **126**, 328–335.

Savithri, H. S., Munshi, S. K., Suryanarayana, S., Divakar, S. & Murthy, M. R. N. (1987). *J. Gen. Virol.* **68**, 1533–1542.

Suryanarayana, S., Appaji Rao, N., Murthy, M. R. N. & Savithri, H. S. (1989). *J. Biol. Chem.* **264**, 6273–6279.

Suryanarayana, S., Jacob, A. N. K. & Savithri, H. S. (1988). *Indian J. Biochem. Biophys.* **25**, 580–584.

Acta Cryst. (1990). B**46**, 567–572

Structure of 1,2-Dinitrobenzene

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Abstract

$C_6H_4N_2O_4$, $M_r = 168\cdot11$, monoclinic, $P2_1/c$, $a = 7\cdot945\,(5)$, $b = 12\cdot975\,(8)$, $c = 7\cdot421\,(5)$ Å, $\beta = 111\cdot88\,(1)^\circ$, $V = 709\cdot90$ Å^3, $Z = 4$, D_m (flotation at 290 K) $= 1\cdot565$, $D_x = 1\cdot573$ g cm^{-3}, λ(Mo $K\alpha$) $= 0\cdot71069$ Å, μ(Mo $K\alpha$) $= 0\cdot90$ cm^{-1}, $F(000) = 344$, room temperature, $R_F = 0\cdot0541$ for 1444 observed reflections. The molecules are stacked along [001], with approximate hexagonal close packing of the stacks. The two nitro groups are twisted out of the mean plane of the benzene ring by angles of $\sim 41^\circ$, the molecule having very nearly $C_2 - 2$ symmetry. The anisotropic displacements of the atoms have been analysed in terms of the translational, librational and screw motions of the molecule as a unit, with the addition of internal torsional oscillations of the nitro groups about the C—N bonds. The motion-corrected molecular dimensions are in good agreement with standard values, confirming that

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there is very little conjugation between the nitro groups and the benzene ring.

Introduction

Although the crystal structures of 1,4- and 1,3-dinitrobenzene have been known for many years [*para* isomer: James, King & Horrocks (1935), Di Rienzo, Domenicano & Riva di Sanseverino (1980); *meta* isomer: Archer (1946), Colapietro, Di Rienzo, Domenicano, Portalone & Riva di Sanseverino (1977)], only cell dimensions have been reported for the *ortho* isomer [Hertel & Schneider (1930), in reasonable agreement with our values; also by Chaudhury & Talapatra (1955), in poor agreement with our values]. One of us tried unsuccessfully to determine the structure in his first attempt at crystal structure analysis (Herbstein, 1948) and then returned to it recently when searching for a suitable demonstration structure for a course project. Remarkably, the crystal structure had been ignored for 40 years; the only compound containing *ortho*-nitro groups whose structure has been determined is 4-chloro-1,2-dinitrobenzene, which has three polymorphs (Groth, 1917, Vol. IV, p. 38). The structures of the β- and γ-polymorphs have been reported by Wilkins & Small (1985; abbreviated as WS85). The *o*-dinitrobenzene molecule has, of course, been studied over the years by a number of physical techniques, and some of these results are discussed below.

1,2-Dinitrobenzene was first crystallized by Zincke in 1874 (crystals, 6–8 mm thick and up to 15 mm long, were obtained from acetone–chloroform) and studied crystallographically by Bodewig in 1876. The axial ratios reported by Groth (1917, Vol. IV, pp. 13–14), who gives references to the earlier studies, agree well with those calculated from our cell dimensions reported below (Groth $a{:}b{:}c = 0{\cdot}6112{:}1{:}0{\cdot}5753$, $\beta = 112{\cdot}12°$; our values $0{\cdot}6123{:}1{:}0{\cdot}5719$, $\beta = 111{\cdot}88°$). We have not attempted to check Groth's report of $\{010\}$, $\{110\}$, $\{001\}$, $\{011\}$, $\{11\bar{1}\}$ and $\{\bar{1}02\}$ faces.

Experimental

The compound was recrystallized twice from 95% ethanol. A yellow prism (m.p. 389–389·5 K, lit. 391 K) of dimensions 0·60 mm (along [001]), 0·34 mm (along [010]) and 0·26 mm (along [100]) was mounted on a Philips PW 1100 four-circle diffractometer (graphite-monochromated Mo $K\alpha$ radiation) with [001] approximately along the φ axis. Unit-cell dimensions were determined from 25 reflections with $30 < 2\theta < 43°$. Intensities of 2208 reflections ($5 \leq 2\theta \leq 50°$) were measured by the ω-scan method and merged ($R_{\text{int}} = 0{\cdot}0248$) to give 1444 reflections used in the structure analysis. Intensities of three standard reflections were measured at intervals of 120 min; corrections were made for a linear decline of $\sim 5\%$ during the course of the measurements and for absorption (maximum and minimum transmission factors = 0·978 and 0·970). The structure was solved by direct methods using *SHELXS*86 (Sheldrick, 1986) and refined by *SHELX*77 (Sheldrick, 1977) to R_F (= wR) = 0·0541, using all 1444 independent measured reflections; anisotropic displacement factors were refined for non-H atoms and isotropic displacement factors for H atoms. Unit weights were used throughout as tests showed that no advantage was obtained by using a more sophisticated weighting scheme. The largest value of $|\Delta/\sigma|$ in the final refinement cycle was 0·007 (mean value 0·0004), and $\Delta\rho_{\max}$ and $\Delta\rho_{\min}$ in the corresponding difference map were 0·19 and $-0{\cdot}21$ e Å^{-3} respectively. Omission of reflections with $F_o < 1{\cdot}5\sigma(F_o)$ reduced the number included in the refinement to 1333 and R_F to 0·0505. Atomic parameters from the 1444-reflection refinement (Tables 1 and 2) were used in all calculations.*

Table 1. *Atomic coordinates* ($\times 10^4$) *for o-DNB*

	x	y	z
C(1)	3727 (2)	7836 (2)	1858 (3)
C(2)	2208 (3)	8435 (1)	1578 (3)
C(3)	557 (3)	7980 (2)	1261 (3)
C(4)	430 (3)	6918 (2)	1215 (4)
C(5)	1928 (4)	6321 (2)	1462 (3)
C(6)	3595 (3)	6778 (2)	1793 (3)
N(1)	5541 (2)	8299 (2)	2400 (3)
O(1)	6558 (2)	7918 (2)	1688 (4)
O(2)	5921 (2)	9008 (2)	3566 (3)
N(2)	2262 (3)	9565 (1)	1474 (3)
O(3)	3127 (3)	9948 (1)	584 (3)
O(4)	1372 (3)	10048 (1)	2224 (3)
HC(3)	−446 (36)	8436 (21)	1168 (37)
HC(4)	−704 (37)	6596 (21)	1099 (38)
HC(5)	1815 (33)	5596 (20)	1513 (35)
HC(6)	4604 (39)	6390 (22)	2005 (41)

Table 2. *Anisotropic displacement parameters* (Å^2 $\times 10^4$) *for* C, N, O *atoms and isotropic displacement parameters* (Å^2 $\times 10^4$) *for* H *atoms of o-DNB*

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C(1)	326 (9)	425 (10)	391 (11)	37 (8)	147 (8)	7 (8)
C(2)	379 (9)	354 (9)	354 (10)	2 (8)	147 (8)	15 (8)
C(3)	365 (10)	551 (13)	482 (13)	63 (10)	177 (9)	27 (9)
C(4)	453 (12)	571 (14)	560 (15)	65 (11)	181 (11)	−140 (10)
C(5)	708 (16)	378 (11)	487 (14)	24 (10)	216 (11)	−83 (11)
C(6)	520 (13)	433 (11)	515 (14)	47 (10)	225 (11)	129 (10)
N(1)	336 (9)	607 (13)	720 (14)	141 (11)	131 (9)	5 (9)
O(1)	466 (10)	1103 (17)	1307 (20)	71 (15)	512 (12)	63 (11)
O(2)	533 (11)	734 (13)	881 (15)	−51 (11)	44 (10)	−193 (9)
N(2)	522 (11)	387 (9)	515 (12)	−2 (8)	91 (9)	44 (8)
O(3)	781 (12)	481 (10)	809 (13)	109 (9)	296 (10)	−120 (9)
O(4)	1044 (16)	562 (11)	922 (15)	−113 (10)	440 (13)	247 (11)
HC(3)	757 (83)		HC(4)	782 (85)		
HC(5)	654 (75)		HC(6)	870 (95)		

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* A list of structure factors has been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52843 (10 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Results

o-Dinitrobenzene (*o-DNB*)

The numbering system and molecular dimensions are summarized in Fig. 1; the results of other geometrical calculations are given in Table 3. In the discussion below we assume the e.s.d.'s of the atomic coordinates to be isotropic, and multiply the values given in Table 1 by a factor of 1·5 to take into account the well-established underestimation of e.s.d.'s from the least-squares variance–covariance matrix (Taylor & Kennard, 1986).

The molecular arrangement in the unit cell is shown in Fig. 2. There are only dispersion forces between the molecules which are stacked along [001] in an approximate hexagonal close-packed arrangement. The mean interplanar distance between the planes of the benzene rings of adjacent molecules in a stack is $c/2 = 3{\cdot}7$ Å.

γ-4-*Chloro*-1,2-*dinitrobenzene* (γ-*CDNB*)

As we shall make comparisons with this molecule as found in the γ-polymorph (the results for the β-polymorph are not precise enough for consideration here) some comments are made (after correspondence with Dr R. W. H. Small) about the structure as reported. The H-atom coordinates in Table 1 of WS85 are calculated values and thus e.s.d.'s should not have been appended. The deviations from the best plane of the benzene ring given in Table 3 of WS85 are (somewhat) incorrect; correct values are given in our Table 3. Our bond lengths and angles agree with those of WS85 to within 0·001 Å and 0·1°; torsion angles agree within 0·1–0·4° apart from τ[C(6)C(1)N(1)O(2)] which was given by WS85 as − 136·7 (5)° and calculated by us as − 139·4°. The fractional e.s.d.'s of the cell dimensions given by WS85 are ~ 1 in 500, compared to ~ 1 in 1000 for *o*-dinitrobenzene. It would seem realistic to multiply the coordinate e.s.d.'s given in Table 1 of WS85 by a factor of 1·75 in order to take this into account in addition to the underestimation noted above. Our discussion is based on these revisions.

Table 3. *Definition of planes through various groups of atoms in the o-DNB and γ-CDNB molecules*

The best planes were calculated with respect to the starred atoms, using *GEOM* and are referred to orthogonal axes *X*, *Y* and *Z* (measured in Å) where $X\|\mathbf{a}$, $Y\|\mathbf{b}$, $Z\|\mathbf{c}^*$.

	o-DNB	γ-CDNB
Cl	—	0·018
C(1)*	0·006	0·002
C(2)*	−0·005	−0·001
C(3)*	−0·001	−0·001
C(4)*	0·006	0·001
C(5)*	−0·005	0·000
C(6)*	−0·001	−0·002
N(1)	0·143	0·110
N(2)	−0·112	−0·125
O(1)	−0·503	−0·483
O(2)	0·922	0·830
O(3)	−0·883	−0·957
O(4)	0·542	0·585

o-DNB

(1) The equation of the best ring plane is:
$0{\cdot}2088X - 0{\cdot}0167Y + 0{\cdot}9778Z = 0{\cdot}6678$ Å.

(2) The equation of the best plane through atoms C(1), N(1), O(1), O(2) is:
$-0{\cdot}3478X + 0{\cdot}6451Y - 0{\cdot}6803Z = 5{\cdot}4189$ Å.

(3) The equation of the best plane through atoms C(2), N(2), O(3), O(4) is:
$0{\cdot}8026X + 0{\cdot}0288Y + 0{\cdot}5908Z = 1{\cdot}9342$ Å.
The angle between planes (1) and (2) is 41·5° and that between planes (1) and (3) is 41·4°.

γ-CDNB

(1) The equation of the best ring plane is:
$-0{\cdot}6595X + 0{\cdot}6589Y - 0{\cdot}3619Z = -3{\cdot}1508$ Å.

(2) The equation of the plane through atoms C(1), O(1), O(2) is:
$0{\cdot}1556X - 0{\cdot}6317Y + 0{\cdot}7594Z = 4{\cdot}6882$ Å.
N(1) deviates by 0·018 Å from this plane.

(3) The equation of the plane through atoms C(2), O(3), O(4) is:
$0{\cdot}6683X + 0{\cdot}0258Y + 0{\cdot}7434Z = 5{\cdot}1756$ Å.
N(2) deviates by −0·022 Å from this plane.

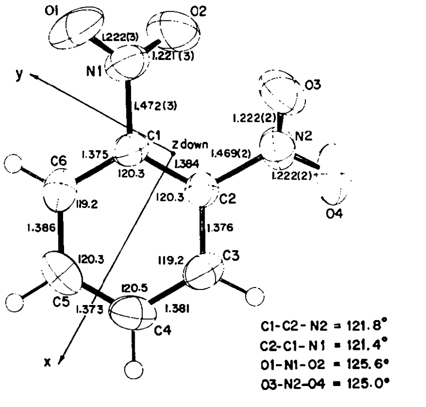

Fig. 1. *ORTEP* (Johnson, 1965) diagram of the projection of the molecule onto the plane of the benzene ring; 50% probability ellipsoids are used. The numbering system (H atoms are numbered according to the C atoms to which they are bonded) and selected bond distances (Å) and angles (°) (uncorrected for anisotropic displacement effects) are shown. The e.s.d.'s obtained *from the least-squares refinement* are 0·003 Å for C—C bonds, 0·002—0·003 Å for C—N and N—O bonds, 0·2° for bond angles, and 0·4° for torsion angles involving only non-H atoms. The C—H bond lengths range from 0·91 to 0·98 Å, with $\sigma[d(\text{C—H})] \simeq 0{\cdot}03$ Å and $\sigma(\angle\text{C—C—H}) \simeq 1{\cdot}9°$. The endocyclic torsion angles around the ring, starting from that about the C(1)—C(2) bond, are 1·0, −0·4, −0·7, 1·1, −0·5 and −0·6°. The inertial axes and centre of gravity are shown; the coordinates of the centre of mass with respect to the crystal system are $x = 0{\cdot}3234$, $y = 0{\cdot}8366$, $z = 0{\cdot}1788$.

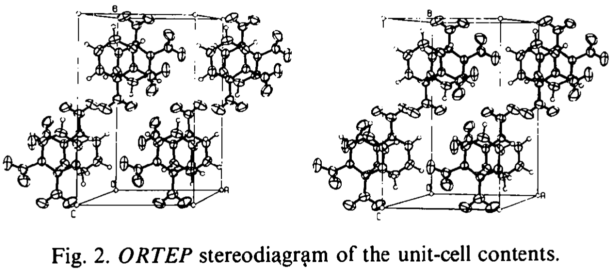

Fig. 2. *ORTEP* stereodiagram of the unit-cell contents.

Discussion

We shall discuss the *o*-DNB molecular structure in its own right and also make comparisons with γ-CDNB; the same numbering systems have been used for both molecules. The results for *o*-DNB appear to be sufficiently precise to demonstrate small distortions of the molecule from a model of assumed symmetry C_2. The *ORTEP* diagram in Fig. 1 shows that there is considerable anisotropic thermal displacement of the *o*-DNB molecule as a whole and additionally of the two nitro groups. The first part of the discussion is based on atomic parameters uncorrected for anisotropic displacement, while this is taken into account in the following section.

Molecular structure without consideration of anisotropic displacements

The overall conformation is clearly determined by the disposition of the two *ortho*-nitro groups, which are rotated about the C—N bonds in the same sense and to almost the same amount. These rotations bring atoms O(2) and O(3) into contact, the distance between them being 2·77 Å which is close to the standard van der Waals diameter of oxygen [2·8 Å from Table 7.2 of Dunitz (1979)]; there are also close contacts between N(1) and N(2) [2·94 Å, approaching the standard van der Waals diameter of nitrogen which is 3·0 Å (Dunitz, 1979)], and between pairs of non-bonded N and O atoms $\{d[\mathrm{N(1)\cdots O(3)}] = 2{\cdot}85$, $d[\mathrm{N(2)\cdots O(2)}] = 2{\cdot}84$ Å$\}$. Much the same situation occurs in γ-CDNB $\{$*e.g.* $d[\mathrm{O(2)\cdots O(3)}] = 2{\cdot}79$ Å$\}$.

The benzene ring in *o*-DNB is significantly non-planar, although to a very small extent. The sum of the squared deviations is 119×10^{-6} Å^2, while the e.s.d. in one direction is 0·0038 Å. Thus $\chi^2 = \sum(\Delta/\sigma)_i^2 = 8{\cdot}2$; on two degrees of freedom $(6-4)$ this is significant at about the 98·5% level. The deviations from planarity are given in Table 3, from where it will be seen that the C atoms follow (slightly) the N atoms to which they are bonded. In a (very considerable) extension of the nomenclature used for saturated rings, we can describe the benzene ring as having an almost flat twist-boat form, ${}^2T_4$ according to Fig. 1 of Boeyens (1978). The benzene ring in γ-CDNB is not significantly distorted from planarity $(\chi^2 = 0{\cdot}5)$.

The two N atoms in *o*-DNB are displaced out of the ring plane by nearly equal but opposite amounts. The angles N(1)—C(1)—C(2) and N(2)—C(2)—C(1) are larger than 120° by 1·4 and 1·8°, and so the two N atoms are slightly splayed apart to 2·94 Å, whereas the distance in a hypothetical planar molecule with 120° bond angles would be 2·85 Å. The corresponding distance in γ-CDNB is 2·96 Å. The two N atoms deviate significantly from the planes through the three atoms to which they are bonded [N(1): $\Delta/\sigma = 0{\cdot}015/0{\cdot}0038 = 3{\cdot}9$; N(2): $\Delta/\sigma = 0{\cdot}020/0{\cdot}0038 = 5{\cdot}3$]; thus the N atoms are very slightly pyramidal. The corresponding deviations in γ-CDNB are 0·018 and −0·022 Å but these are not significant as $\sigma \simeq 0{\cdot}007$ Å.

Substituents are known to introduce dimensional distortions into benzene rings; it is generally considered easier to establish changes in bond angles than in bond lengths unless coordinates corrected for thermal motion are available (Domenicano, Vaciago & Coulson, 1975). We have examined our present results to see whether dimensional distortions can be detected. The mean bond length in the benzene ring of *o*-DNB is $1{\cdot}379_2\,(0{\cdot}005_3)$ Å; the bracketed value is the sample $(N-1)$ standard deviation, which is close to the adjusted value of the experimental bond-length standard deviation $(= 1{\cdot}5 \times 0{\cdot}003 = 0{\cdot}004_5$ Å). We take as our null hypothesis that the bond lengths in the benzene ring are all equal; $\chi^2 = \sum(\Delta/\sigma)_i^2 = 138{\cdot}8/(5)^2 = 5{\cdot}55$, which is well outside the critical region on five degrees of freedom, leading to acceptance of the null hypothesis. An alternative hypothesis about the bond lengths could be that these are grouped shorter–longer– ... around the ring, with the mean length of the shorter bonds as $1{\cdot}374_7(0{\cdot}001_5)$ Å and of the longer bonds $1{\cdot}383_7(0{\cdot}002_5)$ Å [again the bracketed values are the sample $(N-1)$ standard deviations]. The means are significantly different at the 99% level; whether this conclusion has any chemical significance is another matter. Bond angles in the benzene ring can be tested in an analogous manner, taking as our null hypothesis that they are all equal; $\chi^2 = \sum(\Delta/\sigma)_i^2 = 1{\cdot}8/(0{\cdot}2)^2 = 45$, which is well within the critical region, leading to the conclusion that the bond angles differ significantly from 120°. Squeezing the benzene ring along the X inertial axis by 0·01 Å will give the observed changes in bond angles at C(3) and C(6). The bond lengths in γ-CDNB are not significantly different from their mean value of 1·383 Å but the bond angles do differ significantly from 120°.

Distortions from C_2 symmetry for *o*-DNB and γ-CDNB are shown in Table 4. Differences in the deviations from planarity are significant for both molecules, but differences in torsion angles of the nitro groups are significant only for γ-CDNB.

Molecular structure taking anisotropic displacements of the atoms into account

The basic theory has been described by Dunitz (1979) and more recent developments by Dunitz, Maverick & Trueblood (1988) and Dunitz, Schomaker & Trueblood (1988). We start by considering the $\Delta_{A,B}$ $(= z_{A,B}^2 - z_{B,A}^2)$ values for *o*-DNB where $z_{A,B}^2$ is the mean-square displacement amplitude of atom A in the direction of B. For a rigid

Table 4. *Comparison of geometrical parameters showing deviations from C_2 symmetry in o-DNB and γ-CDNB*

(*a*) Deviations (Å) from planarity ($\delta = ||\Delta_1| - |\Delta_2||$)

	o-DNB			γ-CDNB		
	Δ_1	Δ_2	δ/σ	Δ_1	Δ_2	δ/σ
N(1), N(2)	0·143	−0·112	8·3	0·110	−0·125	2·1
O(1), O(4)	−0·503	0·542	10·3	−0·483	0·585	15·6
O(2), O(3)	0·922	−0·883	10·3	0·830	−0·957	18·1

(*b*) Torsion angles (°) ($\delta = |\tau_1 - \tau_2|$)

	o-DNB		γ-CDNB	
	τ_1,τ_2	δ/σ	τ_1,τ_2	δ/σ
C(6)—C(1)—N(1)—O(1)	42·6 (4)	2·0	37·5 (9)	4·4
C(3)—C(2)—N(2)—O(4)	41·8 (4)		33·4 (9)	
C(2)—C(1)—N(1)—O(2)	39·5 (4)	2·5	41·5 (9)	12·5
C(1)—C(2)—N(2)—O(3)	40·5 (4)		44·6 (9)	

Table 5. *Results for the calculations of anisotropic molecular and nitro-group displacement parameters for o-DNB at* 298 K

(*a*) The rigid-body motion of the molecule as a whole

Librational, translational and screw tensors in the inertial frame (Fig. 1)

L (rad²)	0·00820	0·00142	0·00054
		0·00490	0·00270
			0·00670
T (Å²)	0·03818	0·00145	−0·00109
		0·03535	−0·00110
			0·03408
S (rad Å)	0·00020	−0·00043	0·00226
	0·00166	−0·00313	0·00409
	−0·00029	−0·00345	0·00293

(Eigenvalues)$^{1/2}$ and eigenvectors of *L* and *T* in the inertial frame

*L*1	5·66°	0·65699	0·50397	0·56069
*L*2	4·87	0·73629	−0·26917	−0·62082
*L*3	3·04	−0·16195	0·82071	−0·54791
*T*1	0·198 Å	0·87193	0·40636	−0·27316
*T*2	0·187	−0·48539	0·79068	−0·37313
*T*3	0·183	0·06436	0·45793	0·88666

(*b*) Alternative description of the rigid-body motion in terms of the *L*1, *L*2, *L*3 axes (**L** frame)

Shifts of the origin required to symmetrize **S** (Å)

$\rho_{L1} = 0·249$ $\rho_{L2} = 0·599$ $\rho_{L3} = -0·128$

New **S** and **T** tensors

S (rad Å)	0·00153	−0·00036	−0·00024
		−0·00003	0·00110
			−0·00150
T (Å²)	0·03496	0·00250	0·00258
		0·03657	−0·00047
			0·03066

Displacements (Å) of the libration axes from the origin of the inertial frame and the screw pitches along these axes

*L*1	0	0·624	−0·165	0·156
*L*2	0·401	0	−0·077	−0·004
*L*3	−0·140	0·515	0	−0·532

molecule $\Delta_{A,B} = 0$, while Hirshfeld (1976) has suggested that for pairs of *bonded* atoms as heavy as C, $\Delta_{A,B}$ should be less than ~10 pm² for intensity measurements of adequate quality. The selected values shown in Fig. 3 indicate that the benzene ring of *o*-DNB can, as a first approximation, be considered to behave as a rigid body but this does not hold for the two nitro groups. Within each C—NO_2 group the N atom has a large and roughly circular displacement within its surrounding C,O,O triangle. The large $\Delta_{A,B}$ values for O(3) with respect to N(1) and for O(2) with respect to N(2) should also be noted. Using the program *THMA*11 (version of 15 April, 1987) we first treated the whole molecule as a single rigid group; this gave $R(U_{ij})$* = 0·079 (unit weights were used); the larger values of ΔU_{ij}† appeared for the atoms of the nitro groups. We then allowed the two nitro groups to librate internally about their C—N bonds in addition to the rigid-body motion of the molecule as a whole and this reduced $R(U_{ij})$ to 0·043; the values of ΔU_{ij} were now distributed roughly equally over all the atoms. The r.m.s. value of $\Delta U_{ij}{}^2$ was 0·0020 Å², while the e.s.d. of ΔU_{ij} was ~0·0026 Å² (both in the crystal system). We give detailed results (Table 5) only for this latter calculation. Correlations between overall and internal motions were not included. The eigenvectors of the translational tensor are within ~30° of the inertial axes but the axes of libration do not show any clear relation to the inertial axes. The translational tensor is nearly isotropic and hence its eigenvectors are determined with limited precision. The librational tensor is appreciably anisotropic and hence its eigenvectors will be reasonably well defined. The libration amplitudes of the two nitro groups are: NO_2 at C(1) 4·5°, NO_2 at C(2) 5·4°.

The bond lengths have been corrected for the librational motion of the molecule as a whole (0·008–0·010 Å) and also for the torsional motion of the nitro groups (0·010–0·011 Å); the corrected values are given in Table 6. The mean value of the C—C bond length in the benzene ring is 1·389 Å; the values

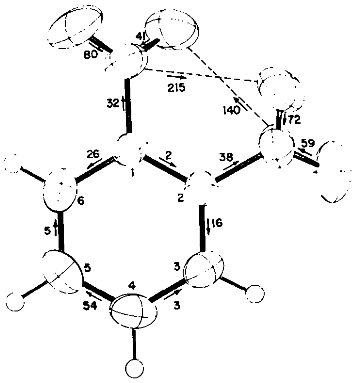

Fig. 3. $\Delta_{A,B}$ values (pm²) for *o*-DNB. The atom at the side of the arrowhead has the larger mean-square displacement amplitude along the interatomic direction. The broken lines show two pairs of nonbonded directions for which large $\Delta_{A,B}$ values are found {*d*[N(1)···O(3)] = 2·85; *d*[N(2)···O(2)] = 2·84 Å}.

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* $R(U_{ij}) = \{\sum[U_{ij}^2(\mathrm{obs}) - U_{ij}^2(\mathrm{calc})]/\sum[U_{ij}^2(\mathrm{obs})]\}^{1/2}$.

† $\Delta(U_{ij}) = U_{ij}(\mathrm{obs}) - U_{ij}(\mathrm{calc})$.

Table 6. *Bond lengths* (Å) *in o-DNB after correction for anisotropic displacement*

C(1)—C(2)	1·395	C(1)—N(1)	1·482
C(1)—C(6)	1·384	N(1)—O(1)	1·243
C(2)—C(3)	1·386	N(1)—O(2)	1·240
C(3)—C(4)	1·389	C(2)—N(2)	1·478
C(4)—C(5)	1·384	N(2)—O(3)	1·241
C(5)—C(6)	1·396	N(2)—O(4)	1·244

reported for benzene itself by a number of techniques range from 1·392 to 1·399 Å (Ermer, 1987). The C—N distance is 1·480 (1) Å, in reasonably good agreement with the microwave value for nitrobenzene (1·492 Å; Høg, Nygaard & Sörensen, 1971) and with a calculated value of 1·517 Å (*STO*5G; Politzer, Abrahamsen & Sjoberg, 1984), suggesting "a very minor degree of conjugation between the nitro group and the aromatic ring of nitrobenzene" (Politzer, Lane, Jayasuriyan & Domelsmith, 1987).

Determination of torsion angles of nitro groups by other methods

(i) *Calculations*. Values around 30° were estimated from molecular-mechanics calculations (Dashevskii, Struchkov & Akopyan, 1966), while *ab initio* calculations gave some preference to values of $\sim 55°$ (Palmer, Moyes, Spiers & Ridyard, 1979). These authors also measured the HeI and II photoelectron spectra of *o*-DNB but strong dependence of the energy-level assignments on the conformation complicated the interpretation of the spectra.

(ii) *Spectroscopic methods*. Comparison of the electronic spectra of the *ortho* and *para* isomers of dinitrobenzene gave values of $\sim 30°$ (Yoshida & Takabayashi, 1965). Balakrishnan & Boykin (1985) have suggested, from measurements of the ^{17}O NMR spectra (in solution) of a number of nitro-substituted organic molecules, that $\tau\,(°) = (1{\cdot}29 \pm 0{\cdot}24)\delta - 739$, where δ is the line position in p.p.m. For *o*-DNB at 348 K, $\delta = 609$ p.p.m. and thus $\tau = 46{\cdot}6°$, in reasonble agreement with the present mean value of 41·5°.

(iii) *Gas-phase electron diffraction*. A number of studies have been made of *o*-DNB but we discuss only the most recent (Penionzhkevich, Sadova, Popik, Vilkov & Pankrushev, 1979). The mean bond lengths and some angles are in good agreement with the crystallographic results [C—C = 1·397 (1), C—N = 1·475 (4), N—O = 1·224 (1) Å, $\angle CC_NC$ = 120·4 (3), $\angle$ONO = 124·9 (2)°] but there are differences in the deviations of the N atoms from the benzene plane, where the electron diffraction value (0·046 Å) is less than half the X-ray diffraction values, and in the torsion angles of the nitro groups where the electron diffraction value is 31·1 (6)°. [Note that we have given e.s.d.'s (σ's) in brackets and not 3σ values as in the original paper.]

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References

Archer, E. M. (1946). *Proc. R. Soc. London Ser. A*, **188**, 51–62.

Balakrishnan, P. & Boykin, D. W. (1985). *J. Org. Chem.* **50**, 3661–3663.

Boeyens, J. C. A. (1978). *J. Cryst. Mol. Struct.* **8**, 317–320.

Chaudhury, A. M. & Talapatra, S. K. (1955). *Pak. J. Sci. Res.* **5**, 124–126; *Chem. Abstr.* **49**, 31b.

Colapietro, M., Di Rienzo, F., Domenicano, A., Portalone, G. & Riva di Sanseverino, L. (1977). 4th Eur. Crystallogr. Meet., Oxford. Abstracts, pp. 517–518.

Dashevskii, V. G., Struchkov, Yu. T. & Akopyan, Z. A. (1966). *J. Struct. Chem. USSR*, **7**, 555–561.

Di Rienzo, F., Domenicano, A. & Riva di Sanseverino, L. (1980). *Acta Cryst.* **B36**, 586–591.

Domenicano, A., Vaciago, A. & Coulson, C. A. (1975). *Acta Cryst.* **B31**, 221–234.

Dunitz, J. D. (1979). *X-ray Analysis and the Structure of Organic Molecules.* Ithaca, London: Cornell Univ. Press.

Dunitz, J. D., Maverick, E. F. & Trueblood, K. N. (1988). *Angew. Chem. Int. Ed. Engl.* **27**, 880–895.

Dunitz, J. D., Schomaker, V. & Trueblood, K. N. (1988). *J. Phys. Chem.* **92**, 856–867.

Ermer, O. (1987). *Angew. Chem. Int. Ed. Engl.* **26**, 782 784.

Groth, P. (1917). *Chemische Kristallographie.* Leipzig: Engelmann.

Herbstein, F. H. (1948). MSc Thesis, Department of Physics, Univ. of Cape Town, South Africa.

Hertel, E. & Schneider, K. (1930). *Z. Phys. Chem. (Leipzig) Abt. B*, **7**, 188–209.

Hirshfeld, F. L. (1976). *Acta Cryst.* **A32**, 239–244.

Høg, J. H., Nygaard, L. & Sörensen, G. O. (1971). *J. Mol. Struct.* **7**, 111–121.

James, R. W., King, G. & Horrocks, H. (1935). *Proc. R. Soc. London Ser. A*, **153**, 225–246.

Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.

Palmer, M. H., Moyes, W., Spiers, M. & Ridyard, J. N. A. (1979). *J. Mol. Struct.* **55**, 243–263.

Penionzhkevich, N. P., Sadova, N. I., Popik, N. I., Vilkov, V. V. & Pankrushev, Yu. A. (1979). *J. Struct. Chem. USSR*, **20**, 512–520.

Politzer, P., Abrahamsen, L. & Sjoberg, P. (1984). *J. Am. Chem. Soc.* **106**, 855–860.

Politzer, P., Lane, P., Jayasuriyan, K. & Domelsmith, L. N. (1987). *J. Am. Chem. Soc.* **109**, 1899–1901.

Sheldrick, G. M. (1977). *SHELX*77. Program for crystal structure determination. Univ. of Cambridge, England.

Sheldrick, G. M. (1986). *SHELXS*86. Program for solution of crystal structures from diffraction data. Univ. of Göttingen, Federal Republic of Germany.

Taylor, R. & Kennard, O. (1986). *Acta Cryst.* **B42**, 112–120.

Wilkins, A. & Small, R. W. H. (1985). *Acta Cryst.* **C41**, 1509–1512.

Yoshida, Z. & Takabayashi, F. (1965). *Kogyo Kagaku Zasshi*, **68**, 812–815; *Chem. Abstr.* **63**, 12520e.