# organic compounds

# Dimorphic forms of 3,6-dinitrodurene in a single space group

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3,6-Dinitrodurene (1,2,4,5-tetramethyl-3,6-dinitrobenzene), $C_{10}H_{12}N_2O_4$, has been crystallized in two polymorphic forms which may be distinguished by their colours in the solid state. Polymorph I gives clear colourless prismatic crystals, while polymorph II crystallizes in the dark and under an inert atmosphere as irregular purple blocks. Both forms belong to the space group $C2/c$, with both asymmetric units containing two half-molecules. One molecule is located on an inversion centre and the other lies on a twofold axis. The polymorphism arises from different orientations of the twofold axis: in form I, this axis passes through the mid-points of two C—C bonds of the benzene ring and, as a consequence, all atoms in the asymmetric unit are in general positions. In form II, the N atoms of the nitro groups and the $C_{ipso}$ atoms are located on the binary axis. Comparing phases I and II, slightly different conformations are observed for the nitro substituents, while the stacking structures are very similar.

## Comment

Durene (1,2,4,5-tetramethylbenzene) is a highly symmetric molecule belonging to point group $D_{2h}$ (Prince *et al.*, 1973). Numerous homo-3,6-disubstituted durene derivatives have been prepared, one of the first being 3,6-dinitrodurene, (1), obtained by direct nitration of durene (Smith & Dobrovolny, 1926). A preliminary X-ray characterization of this molecule
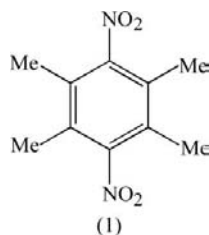
appeared 50 years ago and reported cell parameters and space group (Trotter, 1959). However, for unclear reasons, that characterization was never completed. In the general class of $D_{2h}$-durene derivatives, polymorphism is unusual and has

been clearly described to date only for hexamethylbenzene (Le Maguères *et al.*, 2001). We have now detected that at least two $C2/c$ polymorphs are stabilized for the title molecule, and report here their structures.

The title compound, (1), was initially synthesized as a starting material for the preparation of polyimide membranes intended for gas separation. During the purification of this material, one batch was recrystallized from methanol, affording, as invariably described in the literature, well shaped colourless crystals (polymorph I hereafter). However, another batch, serendipitously left in the dark and under an inert atmosphere, gave irregular purple crystals (polymorph II hereafter). Providing that the crystallizations were carried out as slowly as possible, pure phases were obtained and concomitant polymorphs were not observed.

All $D_{2h}$-durene derivatives previously characterized by X-ray analysis crystallize with the molecule(s) placed on an inversion centre (*e.g.* tetramethylhydroquinone: Pennington *et al.*, 1986; dicyanodurene: Britton & van Rij, 1991). By contrast, the title compound is a $Z' = 1$ structure with two half-molecules per asymmetric unit in both phases. One molecule is located on an inversion centre and the other molecule on a twofold axis. The dimorphism results from the position of the $C_2$ molecule in the cell. Indeed, two special orientations are consistent for this molecule in the space group $C2/c$, assuming an ideal $D_{2h}$ molecular symmetry. The crystallographic twofold axis may correspond to the molecular $C_2$ axis containing the N atoms of the nitro groups, or to the other $C_2$ axis in the same plane and normal to the first. The latter arrangement is found in polymorph I (Fig. 1), while the former is observed in polymorph II (Fig. 2), a situation reminiscent of that reported for another dimorphic $D_{2h}$ molecule, namely 2,3,5,6-tetraphenylpyrazine (Bartnik *et al.*, 1999). As a consequence, all
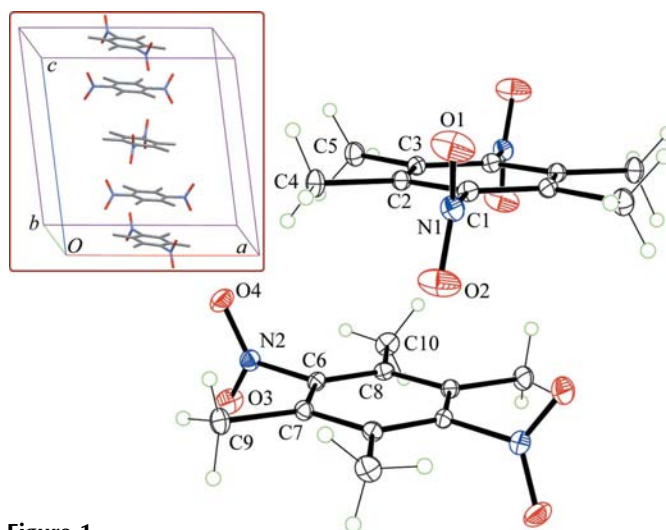


**Figure 1**
The molecular structure of polymorph I. The upper molecule is located on an inversion centre and nonlabelled atoms are generated through the symmetry code $(1 - x, 1 - y, 1 - z)$; the lower molecule is located on a binary axis and the symmetry code for the nonlabelled atoms is $(1 - x, y, \frac{3}{2} - z)$. Displacement ellipsoids are shown at the 20% probability level. The inset shows part of the crystal structure, including one stack of molecules.
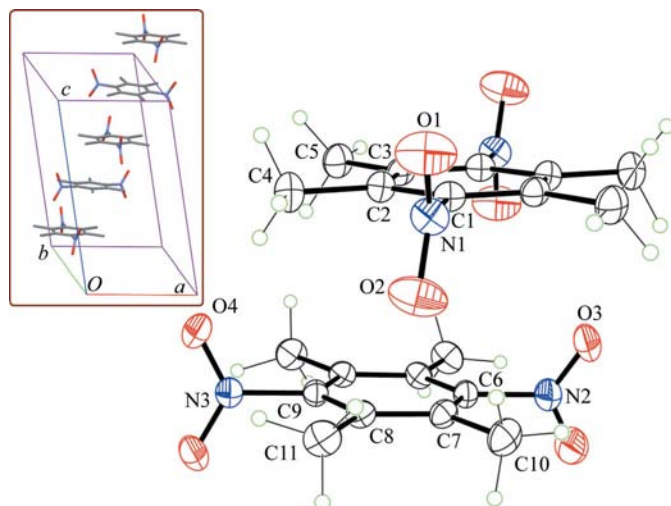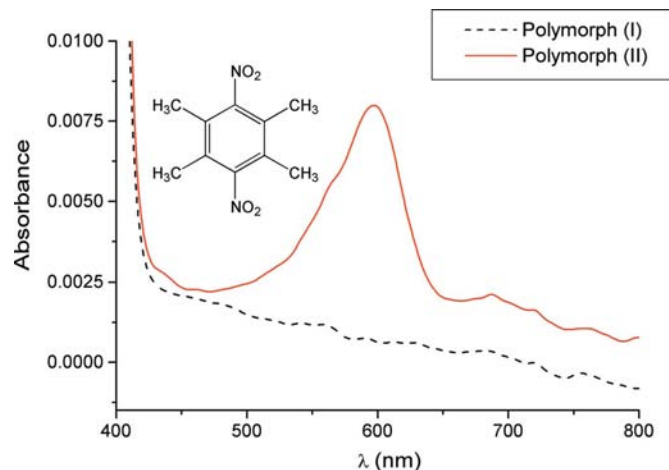
**Figure 2**
The molecular structure of polymorph II. The upper molecule is located on an inversion centre and nonlabelled atoms are generated through the symmetry code ($\frac{1}{2} - x, \frac{1}{2} - y, 1 - z$); the lower molecule is located on a binary axis and the symmetry code for the nonlabelled atoms is ($1 - x, y, \frac{3}{2} - z$). Displacement ellipsoids are shown at the 20% probability level. The minor positions of the disordered methyl H atoms are not shown. The inset shows part of the crystal structure, including one stack of molecules.

atoms in polymorph I are located in general positions, while in polymorph II, atoms C6, C9, N2 and N3 are in special positions. The unit cells have approximately identical parameters and volumes, with a different orientation for the binary axis. Polymorphism in a single space group seems to be a poorly documented occurrence, probably because it is an uncommon phenomenon. It should, however, arise for good reasons rather than on a random basis and thus deserves efforts to be understood. For example, it was recently claimed that a specific crystal nucleation mechanism may be related to the existence of nonconcomitant polymorphs (Burley & Prior, 2006).

Polymorphism does not affect significantly the molecular structure of the title molecule. As expected, the nitro groups are almost perpendicular to the benzene rings in order to avoid steric hindrance with the methyl substituents. Such a resonance inhibition is common in polysubstituted nitrobenzene derivatives (*e.g.* 1,2,4,5-tetrachloro-3,6-dinitrobenzene; Wigand *et al.*, 1987) and is not surprising, as it has been shown that the energy required for tilting a nitro group out of a benzene plane is rather low (Dashevskii *et al.*, 1966). In polymorph I, the dihedral angle between the nitro and benzene mean planes is 85.60 (10)° for the centrosymmetric molecule and 79.76 (8)° in the other molecule. In polymorph II, the centrosymmetric molecule has nitro groups titled as in polymorph I, 86.11 (13)°, while the $C_2$ molecule has two nitro-tilting angles, *viz.* 75.75 (15) and 85.82 (13)°.

Both crystal structures are built up of mixed stacks alternating centrosymmetric and $C_2$ molecules. In polymorph I, stacks run along the [001] axis (Fig. 1, inset), giving a separation between molecules close to $c/4$, as already deduced by Trotter (1959), who noted that reflection (004) has a strong intensity. Actually, centroids of neighbouring benzene rings in polymorph I are separated by 4.238 (1) Å, with a dihedral



**Figure 3**
Electronic spectra of polymorphs I and II of the title compound. Samples were dissolved in tetrahydrofuran and the concentrations were 440 and 630 p.p.m. for I and II, respectively. The figure displays the visible region of the spectra, while the UV region (not shown) features the expected $\pi \to \pi^*$ transitions of the aromatic systems.

angle of 4.01 (5)°. In polymorph II, although the stack orientation deviates from cell axis $c$ (Fig. 2, inset), the geometric parameters are very close to those observed in form I: molecules are separated by 4.285 (1) Å and tilted by 3.99 (5)°. In both forms, nitro groups within a stack adopt a staggered arrangement, minimizing intermolecular hindrance.

Finally, an obvious concern is to explain why, despite so similar molecular and crystal structures, polymorphs I and II present different colours in the solid state. X-ray structures of isomers of the title compound have been reported. *m*-Dinitrodurene is a colourless solid, with molecules packed at a 4.342 Å distance and parallel in a stack (Ori *et al.*, 1989), while *o*-dinitrodurene is reported as a yellow solid, with molecules separated by 4.119 or 4.215 Å (Sgarabotto *et al.*, 1989). In the latter case, the yellow colour is likely a consequence of the shift of the $\pi \to \pi^*$ transition expected for a benzene ring substituted by two $\sigma$-electron-withdrawing chromophores. The situation is completely different in form II of *p*-dinitrodurene, which presents a well defined absorption at $\lambda = 598$ nm, even when highly diluted in tetrahydrofuran (Fig. 3). In the visible range, polymorph I does not absorb at all in solution. On the other hand, $\pi \to \pi^*$ and $n \to \pi^*$ transitions of nitro groups are known to be characterized by low extinction coefficients. We thus assume than some kind of agostic (attractive) interaction allows the molecules to associate as dimers or oligomers in solution in the case of polymorph II, and that such an arrangement survives the nucleation step. The resulting $\pi$–$\pi$ interactions would then account for the visible absorption. Slow crystallization under noncontrolled conditions can produce the colourless polymorph I, indicating that the agostic interactions are low in energy.

## Experimental

Durene (98%, Aldrich), nitric acid (66.5%), sulfuric acid (98.5%), hexane and methanol (99.96%, Baker) were used for the nitration. In a two-necked vessel equipped with a refrigerant, the nitrating

mixture, $HNO_3$:$H_2SO_4$, was prepared in a 4:6 molar ratio. Durene was dissolved in hexane and then added slowly to the reaction vessel under stirring. During the reaction, it is important to check that the temperature does not exceed 313 K. After durene addition was complete, the mixture was stirred for a further 2 h at 313 K. The resulting solid was washed with large amounts of water and recrystallized, first from tetrahydrofuran and then from methanol. Colourless crystals (polymorph I) were obtained from crystallization carried out without special precautions, while using a dark vessel and under an inert atmosphere purple crystals were obtained (polymorph II). Slow crystallization is essential to obtain pure form I or form II crystals. The crystals are air-stable for several months.

## Polymorph I of compound (1)

### Crystal data

| | |
|---|---|
| $C_{10}H_{12}N_2O_4$ | $V = 2119.4\ (3)$ Å$^3$ |
| $M_r = 224.22$ | $Z = 8$ |
| Monoclinic, $C2/c$ | Mo $K\alpha$ radiation |
| $a = 15.1088\ (11)$ Å | $\mu = 0.11$ mm$^{-1}$ |
| $b = 8.9454\ (5)$ Å | $T = 180\ (2)$ K |
| $c = 15.9300\ (13)$ Å | $0.46 \times 0.34 \times 0.13$ mm |
| $\beta = 100.131\ (8)°$ | |

### Data collection

| | |
|---|---|
| Oxford Diffraction Xcalibur diffractometer | 2155 independent reflections |
| | 1551 reflections with $I > 2\sigma(I)$ |
| 7776 measured reflections | $R_{int} = 0.062$ |

### Refinement

| | |
|---|---|
| $R[F^2 > 2\sigma(F^2)] = 0.047$ | 182 parameters |
| $wR(F^2) = 0.130$ | All H-atom parameters refined |
| $S = 1.08$ | $\Delta\rho_{max} = 0.21$ e Å$^{-3}$ |
| 2155 reflections | $\Delta\rho_{min} = -0.19$ e Å$^{-3}$ |

## Polymorph II of compound (1)

### Crystal data

| | |
|---|---|
| $C_{10}H_{12}N_2O_4$ | $V = 2170.8\ (9)$ Å$^3$ |
| $M_r = 224.22$ | $Z = 8$ |
| Monoclinic, $C2/c$ | Mo $K\alpha$ radiation |
| $a = 8.9592\ (19)$ Å | $\mu = 0.11$ mm$^{-1}$ |
| $b = 15.313\ (3)$ Å | $T = 298\ (1)$ K |
| $c = 16.136\ (4)$ Å | $0.40 \times 0.30 \times 0.16$ mm |
| $\beta = 101.300\ (13)°$ | |

### Data collection

| | |
|---|---|
| Bruker $P4$ diffractometer | $R_{int} = 0.036$ |
| 6214 measured reflections | 3 standard reflections |
| 2492 independent reflections | every 97 reflections |
| 1423 reflections with $I > 2\sigma(I)$ | intensity decay: 1.5% |

### Refinement

| | |
|---|---|
| $R[F^2 > 2\sigma(F^2)] = 0.051$ | 48 restraints |
| $wR(F^2) = 0.152$ | All H-atom parameters refined |
| $S = 1.06$ | $\Delta\rho_{max} = 0.19$ e Å$^{-3}$ |
| 2492 reflections | $\Delta\rho_{min} = -0.14$ e Å$^{-3}$ |
| 223 parameters | |

Although polymorph I affords large and well shaped crystals, they are poorly diffracting and data were collected at low temperature (work done in Toulouse). In order to rule out a possible low-temperature phase transition, cell parameters were also measured at 298 K and did not show any symmetry modification. The data for polymorph II were collected at room temperature (work done in Monterrey). In both structures, data resolution allowed accurate positions for all H atoms to be determined, which were then freely refined. In the case of polymorph II, H atoms are disordered over two positions due to a free rotation of the methyl groups about the C—C $\sigma$ bonds. Each part of the disordered groups was restrained to approximate an ideal tetrahedral geometry by restraining C—H and H$\cdots$H distances to a target geometry identical for all methyl groups. C—H bond lengths converged to 1.003 (19)–1.046 (18) Å. Occupancies were refined to common values for all methyl groups, constraining the sum of occupancies in each group to 1. Occupancies converged to 0.621 (12) and 0.379 (12). The same behaviour is probably also present in polymorph I, but limited at 180 (2) K, and methyl groups were eventually refined with nondisordered H atoms. In polymorph I, C—H bond lengths are in the range 0.89 (3)– 1.02 (3) Å. Isotropic displacement parameters for H atoms were refined to a single value in each structure, and converged to 0.071 (2) and 0.071 (3) Å$^2$ for polymorphs I and II, respectively.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2007) for polymorph I; *XSCANS* (Siemens, 1996) for polymorph II. Cell refinement: *CrysAlis RED* (Oxford Diffraction, 2007) for polymorph I; *XSCANS* for polymorph II. Data reduction: *CrysAlis RED* for polymorph I; *XSCANS* for polymorph II. For both polymorphs, program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXL97* and *Mercury* (Macrae *et al.*, 2008); software used to prepare material for publication: *SHELXL97*.

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