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Polymorphism of 1-Chloro-2,4-dinitrobenzene: Structures of α and β Forms

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(*Received* 15 *February* 1990; *accepted* 25 *June* 1990)

Abstract

$C_6H_3ClN_2O_4$, $M_r = 202{\cdot}55$, $\lambda(\text{Mo } K\alpha) = 0{\cdot}7107$ Å. α form: orthorhombic, $Pccn$, $a = 8{\cdot}937\,(5)$, $b = 11{\cdot}035\,(5)$, $c = 15{\cdot}844\,(5)$ Å, $V = 1562{\cdot}5$ Å^3, $F(000) = 816$, $Z = 8$, $D_x = 1{\cdot}721$ Mg m^{-3}, $\mu = 0{\cdot}407$ mm^{-1}, $T = 290$ K. β form: monoclinic, $P2_1/c$, $a = 8{\cdot}91\,(1)$, $b = 6{\cdot}870\,(5)$, $c = 12{\cdot}98\,(1)$ Å, $\beta = 96{\cdot}15\,(5)°$, $V = 790{\cdot}0$ Å^3, $F(000) = 408$, $Z = 4$, $D_x = 1{\cdot}701$ Mg m^{-3}, $\mu = 0{\cdot}403$ mm^{-1}, $T = 290$ K. For the α form, $R = 0{\cdot}045$ for 1474 observed reflexions; for the β form, $R = 0{\cdot}051$ for 976 observed reflexions. Different molecular conformations are found: in the α form the *p*-nitro group is rotated 41·8 (4)° relative to the benzene ring, in the β form the rotation is 68·8 (6)°. The *p*-nitro groups are rotated 11·1 (4) and 13·1 (6)°, in opposite directions. Molecular-energy calculations reveal negligible differences between the two conformations.

Introduction

This investigation is part of a series of studies on compounds which exhibit polymorphism. Two orthorhombic polymorphs of the title compound, with melting points 323 and 316 K, were reported by Groth (1917) who also referred to a more labile third form obtainable from the melt. The three polymorphs, designed α, β and γ, have been characterized by melting points 325, 316 and 300 K (*Dictionary of Organic Compounds*, 1965). The crystal structure of the α form of the title compound has previously been determined by Watson (1960) and Gopalakrishna (1969), both reporting cell dimensions, space group and R values of 0·12 but giving neither atomic coordinates nor bond distances and angles. More recently, however, an accurate determination at 110 K has been reported (Takazawa, Ohba & Saito, 1989).

Experimental

A commercial sample recrystallized from ethanol gave suitable crystals of the α form (melting point 325 K). Upon supercooling the melt to room temperature between a coverslip and microscope slide and pressing hard with a needle, slow polycrystalline growth was initiated. The melting point of this material was 316 K; when small fragments were seeded into a saturated ethanolic solution, single crystals formed. These, assumed to be of the β form, were rapidly removed from solution and dried; if they were left in the solution rapid transformation to the α form occurred. Transition of the β form in the solid state was found to occur when contact was made with crystals of the α form, a cloudy growth emanating from the point of contact. These transformed crystals were found to be the polycrystalline α form. No success was obtained in preparing the γ form from the melt. Space groups and cell dimensions were obtained from Weissenberg photographs taken with Cu $K\alpha$ radiation ($\lambda = 1{\cdot}5418$ Å). More accurate cell dimensions were obtained from 20 measured setting angles on a Stadi-2 two-circle diffractometer in the range $20 < 2\theta < 40°$ using graphite-monochromatized Mo $K\alpha$ radiation. The same instrument was used for intensity measurements, variable ω scan, $2\theta'$ fixed, stationary background count. Crystals were sealed in Lindemann glass capillaries. Separate standards for each layer

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were recorded every ten measurements, any variation being allowed for by linear interpolation. For the α form 2390 intensities (with maximum $\sin\theta/\lambda$ = 0·70 Å^{-1}) were measured using a crystal 0·4 × 0·35 × 0·2 mm for the layers *hk*0 to *hk*20, *h* 0 to 12, *k* 0 to 15. After Lp corrections, merging of equivalent reflexions and omission of 496, with $I < 3\sigma(I)$, considered unobserved, 1474 unique reflexions remained. For the β crystal (which remained metastable for the period of measurement, 12 days) 2105 intensities for layers 0*kl* to 9*kl*, *k* 0 to 8, *l* −16 to 16 (with maximum $\sin\theta/\lambda$ = 0·70 Å^{-1}) were measured and reduced (811 unobserved by the same criteria) to 976 unique values. The phase solutions were obtained by the use of *MULTAN*78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) which gave the positions of all atoms other than H in each structure. *SHELX*76 (Sheldrick, 1976) was used for all other crystallographic calculations; H atoms were found in expected positions on ΔF maps. Full-matrix refinement, based on F, of coordinates and U_{ij} of non-H atoms and isotropic U of H atoms proceeded until parameter shifts were <0·01 e.s.d. for both structures. H atoms were in calculated positions with C—H = 1·08 Å. Interlayer scale factors were refined at an intermediate stage. For the α structure $w = 1{\cdot}0/[\sigma^2(F) + 0{\cdot}0093F^2]$, the final R was 0·045, wR = 0·077 and the largest features on the ΔF map were +0·29 to −0·38 e Å^{-3}. For the β structure the final R was 0·051, $wR = 0{\cdot}071$, $w = 2{\cdot}79/[\sigma^2(F) + 0{\cdot}00087F^2]$, the greatest ΔF map features being +0·30 to −0·30 e Å^{-3}. Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). Atomic parameters are given in Table 1,* and bond distances and angles in Table 2. The molecules, with atomic labelling, are shown in Figs. 1(*a*) and 1(*b*).

Table 1. *Fractional atomic coordinates* (× 10^4, × 10^5 *for* Cl) *and equivalent isotropic vibration parameters* (Å^2 × 10^3, Å^2 × 10^4 *for* Cl)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
(*a*) α form				
Cl	−23029 (9)	4769 (6)	−6764 (3)	617 (6)
C(1)	−1425 (2)	1076 (2)	206 (1)	41 (1)
C(2)	−1822 (2)	749 (2)	1038 (1)	39 (1)
C(3)	−1195 (2)	1321 (2)	1736 (1)	41 (1)
C(4)	−142 (2)	2201 (2)	1584 (1)	40 (1)
C(5)	316 (3)	2524 (2)	773 (1)	44 (1)
C(6)	−351 (3)	1961 (2)	83 (1)	45 (1)
N(1)	−2942 (2)	−194 (2)	1209 (1)	49 (1)
N(2)	476 (3)	2877 (2)	2310 (1)	52 (1)
O(1)	−2884 (3)	−1128 (2)	788 (1)	69 (1)
O(2)	−3835 (2)	6 (2)	1777 (2)	73 (2)
O(3)	−116 (3)	2728 (2)	3001 (1)	77 (2)
O(4)	1529 (2)	3570 (2)	2182 (1)	68 (1)
(*b*) β form				
Cl	41473 (16)	21995 (20)	−7074 (10)	572 (14)
C(1)	3161 (5)	3864 (7)	−39 (3)	39 (4)
C(2)	3019 (5)	3597 (6)	1008 (3)	34 (3)
C(3)	2182 (5)	4839 (6)	1543 (3)	36 (4)
C(4)	1476 (5)	6385 (7)	997 (3)	36 (3)
C(5)	1596 (5)	6692 (7)	−40 (4)	42 (4)
C(6)	2437 (6)	5421 (7)	−558 (3)	47 (4)
N(1)	3770 (5)	1926 (6)	1553 (3)	47 (4)
N(2)	522 (4)	7682 (6)	1547 (3)	44 (3)
O(1)	5126 (5)	1920 (7)	1723 (3)	76 (5)
O(2)	2949 (5)	680 (7)	1840 (4)	93 (6)
O(3)	613 (5)	7566 (6)	2492 (3)	64 (4)
O(4)	−334 (4)	8776 (6)	1036 (3)	67 (5)

Table 2. *Bond lengths* (Å) *and angles* (°)

	α form	β form		α form	β form
C(1)—C(2)	1·412 (3)	1·390 (6)	C(2)—N(1)	1·469 (3)	1·471 (6)
C(2)—C(3)	1·391 (3)	1·371 (6)	C(4)—N(2)	1·478 (3)	1·469 (6)
C(3)—C(4)	1·373 (3)	1·389 (6)	N(1)—O(1)	1·230 (3)	1·205 (5)
C(4)—C(5)	1·395 (3)	1·377 (6)	N(1)—O(2)	1·223 (3)	1·211 (5)
C(5)—C(6)	1·392 (3)	1·373 (7)	N(2)—O(3)	1·226 (3)	1·223 (5)
C(6)—C(1)	1·383 (3)	1·386 (7)	N(2)—O(4)	1·229 (3)	1·216 (5)
C(1)—Cl	1·734 (2)	1·731 (5)			
C(2)—C(1)—Cl	122·8 (2)	120·5 (4)	C(5)—C(4)—N(2)	118·6 (2)	119·4 (4)
C(6)—C(1)—Cl	118·0 (2)	120·0 (4)	C(4)—C(5)—C(6)	119·0 (2)	119·0 (4)
C(6)—C(1)—C(2)	119·1 (2)	119·4 (4)	C(5)—C(6)—C(1)	120·1 (2)	120·1 (4)
C(1)—C(2)—C(3)	121·6 (2)	121·6 (4)	C(2)—N(1)—O(1)	117·7 (2)	119·1 (4)
C(1)—C(2)—N(1)	121·7 (2)	119·3 (4)	C(2)—N(1)—O(2)	117·0 (2)	116·2 (4)
C(3)—C(2)—N(1)	116·7 (2)	119·1 (4)	O(1)—N(1)—O(2)	125·3 (2)	124·6 (5)
C(2)—C(3)—C(4)	117·3 (2)	117·3 (4)	C(4)—N(2)—O(3)	118·1 (2)	117·9 (4)
C(3)—C(4)—C(5)	122·8 (2)	122·5 (4)	C(4)—N(2)—O(4)	117·8 (2)	118·2 (4)
C(3)—C(4)—N(2)	118·5 (2)	118·0 (4)	O(3)—N(2)—O(4)	124·1 (2)	123·9 (4)

Discussion

Bond distances and angles (Table 2) in the α form are similar to those reported by Takazawa, Ohba & Saito (1989) for the same form at 110 K and show small differences which are not significant considering the combined standard deviations. Differences of corresponding interatomic distances in the two polymorphs similarly are not significant, the C(1)—C(2) bond, lengthened in the α form, showing the greatest difference. Both forms show enlarged endocyclic angles (Table 2) at the C atoms adjacent to electron-withdrawing groups, an effect first observed and explained by Carter, McPhail & Sim (1966). Significant differences between corresponding angles in the two forms are to be noted, Cl—C(1)—C(2), C(1)—C(2)—N(1) being greater in the α form than the β with corresponding reductions in Cl—C(1)—C(6) and N(1)—C(2)—C(3). In both forms there are significant displacements of Cl from the benzene nucleus plane, being greater in the α form, 0·138 (2) compared with 0·083 (4) Å in the β form. The O atoms, apart from O(4) of the α form, are also appreciably displaced from the benzene ring planes. This feature is also apparent in the torsion angles. In the case of the dihedral angles between the

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* Lists of structure factors, H-atom coordinates, anisotropic vibrational factors and least-squares planes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53318 (23 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

benzene ring and the *o*-nitro group there is a considerable difference, the values being 41·8 (4)° in the α form and 68·8 (6)° in the β. The smaller rotation in the α form involves a shorter intramolecular Cl···O distance [2·964 (2) Å] than in the β form [3·187 (5) Å] and is accompanied by distortion of the angles at C(1), C(2) and of the C(1)—C(2) bond already mentioned. A similar effect has been reported in the structures of 2,4-dichloro-1,3,5-trinitrobenzene (Holden & Dickinson, 1967) and 2-chloro-1,3,5-trinitrobenzene (Willis, Stewart, Ammon, Preston, Gluyas & Harris, 1971). In both cases Cl is adjacent to two nitro groups, which show different angles of rotation (37, 75 and 33, 81° respectively). For both of these structures the exocyclic angles are distorted so that the Cl is displaced away from the nitro group with the smaller rotation. In the polymorphs of the title compound the dihedral angle between the benzene ring and the nitro group *para* to Cl is 11·1 (4)° in the α form and 13·1 (6)° in the β form, the rotations being in opposite directions.

N(2) of the α form is displaced 0·111 (3) Å from the plane of the benzene ring such that after rotation of the nitro group, O(4) lies only 0·028 (3) Å from that plane. For the β form the displacement of N(2) is 0·060 (6) Å and the rotation in the opposite sense leaves O(4) 0·335 (6) Å from the benzene ring plane.

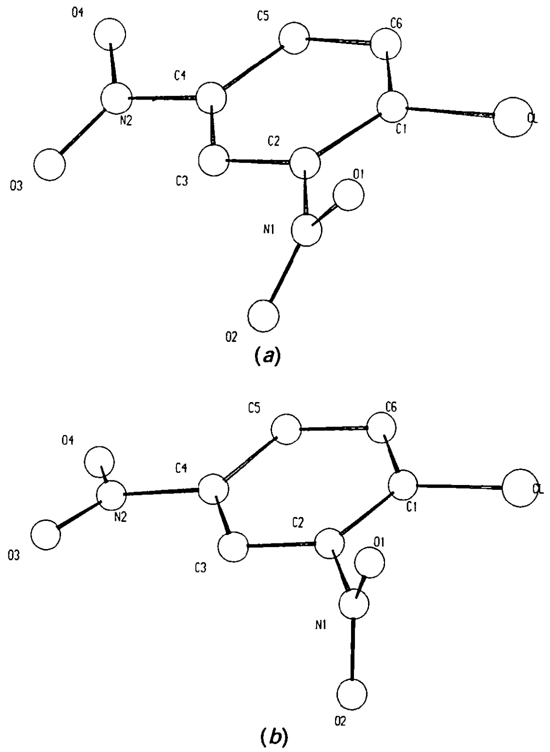

Fig. 1. Molecules of 1-chloro-2,4-dinitrobenzene with atom labelling: (*a*) α form, (*b*) β form.

It would be expected that rotation of nitro groups away from the plane of the benzene ring would be unfavourable unless there were compensating features such as relief of steric interaction with adjacent groups, in this case Cl. A molecular-energy calculation was performed on models with the geometry found in the α and β forms using the *GAMESS* package (Dupuis, Spangler & Wendoloski, 1980) at Manchester Computing Centre with the 72-orbital STO-3G basis set. The result for these two molecules is that the energy of the β conformation is the lower, just 4 kJ mol^{-1}. This indicates a negligible difference in the two energies and suggests that energetically the distortion of the exocyclic angles at C(1) and C(2) in the α form is balanced by the lesser out of plane rotation of the nitro group.

The different molecular conformations give rise to quite different modes of packing in the two structures (Figs. 2 and 3). The closest approaches to Cl in the two structures are from O(4) (*n*-glide related) in the α form [3·348 (2) Å] and from O(1) (centrosymmetrically related) in the β form [3·217 (5) Å], neither being abnormally short. In the α form, pairs of molecules related by the twofold axis parallel to *c* approach to a O(2)···N(2) distance of 2·885 (3) Å, while the closest approach in the β structure [O(2)···N(2) = 2·981 (5) Å] is between *b*-translated molecules. Bearing in mind that the N contacts are both approximately normal to the O—N—O plane, van der Waals separations of 3·05 Å might be expected and there could therefore be weak polar interactions between these pairs.

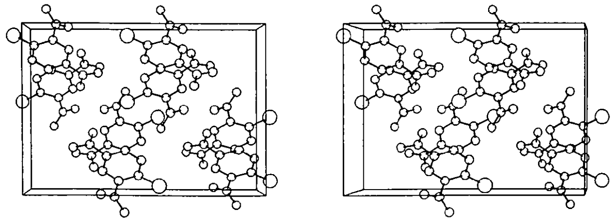

Fig. 2. 1-Chloro-2,4-dinitrobenzene, α form. Molecular packing showing the unit cell projected on 100, with *c* horizontal.

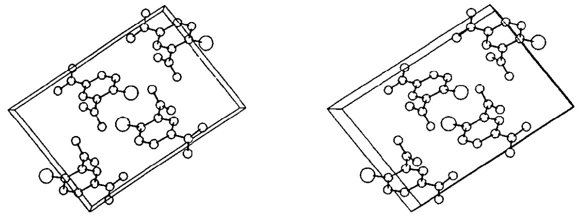

Fig. 3. 1-Chloro-2,4-dintrobenzene, β form. Molecular packing showing the unit cell projected on 010, with *c* nearest horizontal.

The higher density of the α form is consistent with its greater stability. In this compound the polymorphism appears to be a consequence of the similarity of the energies of the two molecular conformations.

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Studies in Crystal Engineering: Topochemical Photodimerization and Structure of *p*-Chlorobenzylidene-DL-piperitone

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(*Received* 2 *April* 1990; *accepted* 18 *June* 1990)

Abstract

3-(*p*-Chlorophenylvinyl)-6-isopropyl-2-cyclohexen-1-one, $C_{17}H_{19}ClO$, $M_r = 274{\cdot}7$, triclinic, $P\bar{1}$, $a = 6{\cdot}636\,(1)$, $b = 10{\cdot}537\,(2)$, $c = 10{\cdot}811\,(3)$ Å, $\alpha = 95{\cdot}31\,(2)$, $\beta = 92{\cdot}60\,(2)$, $\gamma = 100{\cdot}66\,(2)°$, $V = 738{\cdot}2\,(2)$ Å^3, $Z = 2$, $D_m = 1{\cdot}23$, $D_x = 1{\cdot}236$ Mg m^{-3}, Cu $K\alpha$, $\lambda = 1{\cdot}5418$ Å, $\mu = 2{\cdot}09$ mm^{-1}, $F(000) = 292$, $T = 298$ K, $R = 0{\cdot}050$ for 2220 observed reflections. The title compound undergoes a topochemical photodimerization giving an *anti* head-to-tail dimer instead of the *syn* head-to-head dimer expected on the basis of the ability of the chloro group to steer β-type packing. There are no significant Cl···Cl intermolecular interactions. Possible reasons for the observed α-type packing of benzylidenepiperitones are advanced. The low dimer yield is also rationalized.

Introduction

The product obtained from a photochemically induced reaction in the crystalline state is dictated by topochemical factors such as packing, local symmetry and the separation between reactive double bonds (Cohen & Schmidt, 1964; Cohen, Schmidt & Sonntag, 1964; Schmidt, 1964). The type of molecular packing which favours solid-state photochemical reactions has been studied by a number of investigators. A predictive approach, focusing on organic solids, has led to the discovery of many steering groups such as chloro (Schmidt, 1971; Jones, Ramadas, Theocharis, Thomas & Thomas, 1981; Gnanaguru, Murthy, Venkatesan & Ramamurthy, 1984; Desiraju & Sharma, 1986), acetoxy (Ramasubbu, Gnanaguru, Venkatesan & Ramamurthy, 1982; Murthy, Ramamurthy & Venkatesan, 1988) and sulfur (Nalini & Desiraju, 1987). It has been observed that chloro substitution, in particular, favours β-type packing (Ramamurthy & Venkatesan, 1987; Desiraju, 1987) in organic crystals. In order to investigate this chloro-steering effect further and hence facilitate otherwise unattainable photoreactions, we have investigated the photostability of an α-benzylidene-DL-piperitone, which contains two potentially reactive double bonds (Kanagapushpam, Ramamurthy & Venkatesan, 1987).

Experimental

p-Chlorobenzylidene-DL-piperitone (I) and the *o*-chloro derivative (II) were prepared following reported procedures (Read & Smith, 1921). Powdered samples of the compounds were exposed

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