Acta Cryst. (1991). **B47**, 739–742

A Crystal that Hops in Phase Transition, the Structure of *trans,trans,anti,trans,trans*-Perhydropyrene

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(*Received* 1 *October* 1990; *accepted* 12 *April* 1991)

Abstract

trans,trans,anti,trans,trans-Perhydropyrene, (1,2,3,-3a*r*,4,5,5a*t*,6,7,8,8a*t*,9,10,10a*c*,10b*t*,10c*c*)-hexadecahydropyrene, $C_{16}H_{26}$, $M_r = 218{\cdot}38$, monoclinic, $P2_1/c$, $a = 16{\cdot}782\,(7)$, $b = 5{\cdot}447\,(1)$, $c = 16{\cdot}710\,(7)$ Å, $\beta = 120{\cdot}00\,(3)^\circ$, $V = 1322{\cdot}8\,(9)$ Å^3, $Z = 4$, $D_x = 1{\cdot}097$ g cm^{-3}, $\lambda(\mathrm{Cu}\ K\alpha) = 1{\cdot}54182$ Å, $\mu = 4{\cdot}12$ cm^{-1}, $F(000) = 488{\cdot}0$, room temperature, $R = 0{\cdot}052$ for 1355 observed reflections $[I \geq 3\sigma(I)]$. The perhydropyrene molecules are 'planar' in the *trans,trans,anti,trans,trans* configuration, in which all four cyclohexane rings are in the chair conformation and fused in the *trans* form. The two halves of crystallographically independent molecules in the asymmetric unit are tilted with respect to each other at a dihedral angle of 53·9°; the crystal structure is of a layer type with hexagonal packing. Upon heating, a phase transformation occurs at 344·5 K which is associated with jumps of the crystals almost 6 cm high. The transformation is probably of the martensitic type with lateral shifts of lattice planes relative to each other.

Introduction

trans,trans,anti,trans,trans-Perhydropyrene (*ttatt*-perhydropyrene) is the thermodynamically most stable of the 14 diastereoisomers of perhydropyrene (hexadecahydropyrene) (Langer & Lehner, 1973). Investigation under the polarizing microscope and with differential scanning calorimetry of *ttatt*-perhydropyrene crystals led to the discovery of a reversible solid–solid phase transition ($\Delta H \simeq \pm 1{\cdot}4$ kJ mol^{-1}) (Kohne, Praefcke & Mann, 1988). On heating above *ca* 344·5 K as well as on subsequent cooling below *ca* 338·5 K crystals of *ttatt*-perhydropyrene show abrupt vigorous movements and a change of interference colours between crossed polarizers. Each time these two temperatures are passed, and especially in the cooling process, loose uncovered crystals may hop about 6 cm high. This 'colour *and* hopping effect' can be observed many times on taking the same sample of this perhydropyrene stereoisomer through this heating and cooling cycle (Kohne, Praefcke & Mann, 1988). The same phenomenon is observed for a derivative of hexahydroxycyclohexane (*myo*-inositol; Gigg, Gigg, Payne & Conant, 1987; Steiner, Hinrichs, Saenger & Gigg, 1988), which displays this 'colour *and* hopping effect' at two temperatures (Kohne, Praefcke & Mann, 1988). The X-ray crystal structure of *ttatt*-perhydropyrene was determined to provide detailed information about the crystal packing pattern in the unit cell and the conformation of the molecule.

Experimental

Colorless transparent needle-shaped crystals suitable for X-ray diffraction were obtained by slow cooling of hot (~323 K) saturated solutions of *ttatt*-perhydropyrene in ethyl acetate. A crystal with dimensions of 0·20 × 0·20 × 0·50 mm was sealed in a glass capillary and used for all X-ray diffraction measurements. The space group $P2_1/c$ and preliminary unit-cell constants were derived from Weissenberg and precession photographs. The diffraction patterns show strong sixfold rotational symmetry ($a \simeq c$, and $\beta = 120{\cdot}0^\circ$). Data collection was carried out with a Stoe four-circle automated diffractometer with nickel-filtered Cu $K\alpha$ radiation in $\omega/2\theta$ scan mode ($2 \leq \theta \leq 60^\circ$) at room temperature. Accurate unit-cell parameters were obtained by least-squares

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0108-7681/91/050739-04$03.00

refinement based on angular positions of 22 reflections in the 2θ range 27–62°. 1786 reflections were collected in the $\pm h$, $+k$, $+l$ range $-17 \rightarrow 14$, $0 \rightarrow 5$ and $0 \rightarrow 17$; they were merged to yield 1402 unique reflections ($R_{\rm merge} = 0{\cdot}044$), and 1355 reflections were considered observed $[I \geq 3\sigma(I)]$ and used in the refinement. The measured intensities were corrected for Lorentz and polarization effects but not for absorption. The structure was solved using the direct-methods program *SHELXS*86 (Sheldrick, 1986) which provided an *E* map from which all C atoms were located. Their coordinates and anisotropic temperature factors were independently refined by full-matrix least-squares methods with the program *SHELX*76 (Sheldrick, 1976) with minimization of $\sum w(|F_o| - |F_c|)^2$, where $w = 1/(\sigma F_o)^2 = 1{\cdot}0$; all H atoms were put in theoretical positions and their temperature factors refined isotropically. Scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). The final agreement factor for 1355 reflections is $R = 0{\cdot}052$; max. $|\Delta/\sigma| = 0{\cdot}04$; the range of residual Fourier difference electron density is $+0{\cdot}10$ to $-0{\cdot}10$ e Å^{-3}. All calculations were performed on a local MicroVAX 3500 computer. Molecular parameters were calculated with program *PARST* (Nardelli, 1983), drawings were plotted with program *ORTEP*II (Johnson, 1976).

Discussion

A stereoview of the unit-cell contents looking along the *b* axis and a projection onto the *ac* plane to illustrate the hexagonal packing are shown in Fig. 1, and *ORTEP* views of the two crystallographically independent molecules (1) and (2) of *ttatt*-perhydropyrene are shown in Fig. 2. The final fractional coordinates for the C atoms are given in Table 1, the bond lengths and bond angles are listed in Tables 2 and 3.*

In the asymmetric unit there are two halves of crystallographically independent molecules; between them there is no intermolecular C···C contact less than 4 Å. The perhydropyrene molecules are in the *trans,trans,anti,trans,trans* configuration, in which all four cyclohexane rings are in the chair conformation and fused in the *trans* form so that the molecules are almost 'planar', see Fig. 2. The bond lengths and bond angles correspond to the normal values with some differences between equivalent values in molecules (1) and (2); this is expected because the intermolecular forces are only of the van der Waals type. For molecule (1), the average bond length is 1·524 Å with standard deviation $\sigma = 0{\cdot}006$ Å, and the average bond angle is 111·4° with $\sigma = 0{\cdot}6$°; for molecule (2), 1·517 Å, $\sigma = 0{\cdot}007$ Å, and 112·1°, $\sigma = 0{\cdot}8$°. These values are in good agreement with a naturally occurring diisocyanide derivative of perhydropyrene, where the average bond length is 1·53 Å with $\sigma = 0{\cdot}01$ Å (Baker, Wells, Oberhänsli & Hawes, 1976). The average deviations of C atoms from the least-squares planes in molecules (1) and (2) are 0·23 Å with $\sigma = 0{\cdot}02$ Å and 0·22 Å with $\sigma = 0{\cdot}02$ Å, respectively.

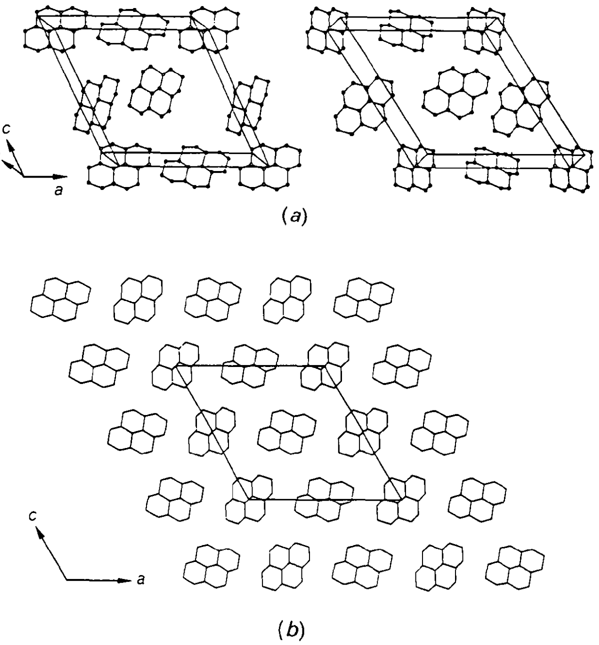

Fig. 1. (*a*) Stereoview of the unit-cell contents, looking along the *b* axis. (*b*) Projection on the *ac* plane to show pseudo-hexagonal packing.

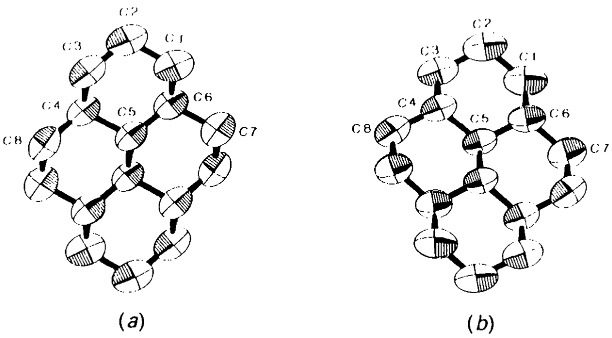

Fig. 2. *ORTEP* view of the two independent molecules in the crystal (30% thermal probability ellipsoids for all atoms). (*a*) Molecule (1). (*b*) Molecule (2).

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* Lists of anisotropic thermal parameters, H-atom coordinates, least-squares planes and deviations from them, non-bonded interatomic distances, and observed and calculated structure-factor amplitudes (Tables 4–8) have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54173 (22 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Fractional coordinates and equivalent thermal parameters* ($Å^2$) *for the* C *atoms with e.s.d.'s in parentheses*

$U_{eq} = (1/3)[U_{22} + 1/\sin^2\beta(U_{11} + U_{33} + 2U_{13}\cos\beta)]$.

	x	y	z	U_{eq}
Molecule (1)				
C1	0·3178 (2)	0·2929 (6)	0·8648 (2)	0·093 (1)
C2	0·2666 (2)	0·2273 (6)	0·9152 (2)	0·108 (1)
C3	0·3329 (2)	0·2074 (6)	1·0183 (2)	0·105 (1)
C4	0·4094 (2)	0·0217 (5)	1·0401 (2)	0·084 (1)
C5	0·4609 (2)	0·0900 (6)	0·9891 (2)	0·073 (1)
C6	0·3957 (2)	0·1130 (5)	0·8854 (2)	0·078 (1)
C7	0·4479 (2)	0·1837 (6)	0·8362 (2)	0·091 (1)
C8	0·4747 (2)	0·0037 (6)	1·1428 (2)	0·100 (1)
Molecule (2)				
C1	0·1785 (2)	0·1908 (6)	0·5459 (2)	0·103 (1)
C2	0·2271 (2)	−0·2329 (6)	0·6491 (2)	0·103 (1)
C3	0·1579 (2)	0·2545 (6)	0·6822 (2)	0·095 (1)
C4	0·0866 (2)	−0·4498 (5)	0·6309 (2)	0·079 (1)
C5	0·0370 (2)	−0·4050 (6)	0·5267 (2)	0·073 (1)
C6	0·1047 (2)	0·3802 (5)	0·4919 (2)	0·083 (1)
C7	0·0543 (2)	−0·3326 (6)	0·3881 (2)	0·099 (1)
C8	0·0188 (2)	−0·4787 (6)	0·6648 (2)	0·099 (1)

Table 2. *Bond lengths* (Å) *for the* C-*atom skeleton with e.s.d.'s in parentheses*

Atoms marked ′ are related by symmetry, for molecule (1): $1 - x$, $-y$, $2 - z$; for molecule (2): $-x$, $-1 - y$, $1 - z$.

	Molecule (1)	Molecule (2)
C1—C2	1·517 (4)	1·513 (4)
C1—C6	1·530 (3)	1·517 (4)
C2—C3	1·519 (4)	1·522 (4)
C3—C4	1·530 (4)	1·509 (4)
C4—C5	1·534 (3)	1·530 (3)
C4—C8	1·513 (3)	1·512 (4)
C5—C6	1·525 (3)	1·520 (3)
C5—C5′	1·530 (5)	1·518 (5)
C6—C7	1·521 (3)	1·526 (3)
C7—C8′	1·523 (4)	1·505 (4)
C8—C7′	1·523 (4)	1·505 (4)

The packing of the molecules in the crystal lattice is of a corrugated layer type, with layers arranged parallel to the *ac* plane. Adjacent layers are related by the 2_1 screw axis and the glide plane along *c*. In the projection along *b*, the pseudo-hexagonal arrangement of the molecules is apparent (Fig. 1*b*), which was also indicated in *h*0*l* X-ray photographs. The two independent molecules are not parallel but at a dihedral angle of 53·9° between their least-squares planes. The thermal motion of the two molecules is comparable as shown by the orientation of the atomic thermal ellipsoids, see Fig. 2, the main vibrational direction is 'across' the molecules, approximately along the C6–C7′ vector.

Table 3. *Bond angles* (°) *for the* C-*atom skeleton with e.s.d.'s in parentheses*

Atoms marked ′ are related by symmetry, for molecule (1): $1 - x$, $-y$, $2 - z$; for molecule (2): $-x$, $-1 - y$, $1 - z$.

	Molecule (1)	Molecule (2)
C2—C1—C6	112·5 (2)	113·0 (2)
C1—C2—C3	110·5 (2)	110·7 (3)
C2—C3—C4	111·7 (2)	112·4 (2)
C3—C4—C5	110·3 (2)	111·1 (2)
C3—C4—C8	112·1 (2)	113·1 (2)
C5—C4—C8	111·3 (2)	111·2 (2)
C4—C5—C6	111·6 (2)	111·5 (2)
C1—C6—C5	110·9 (2)	112·2 (2)
C1—C6—C7	112·0 (2)	112·6 (2)
C5—C6—C7	110·8 (2)	110·9 (2)
C4—C5—C5′	111·5 (2)	112·4 (2)
C6—C5—C5′	111·5 (2)	112·6 (2)
C6—C7—C8′	111·6 (2)	112·2 (2)
C4—C8—C7′	111·8 (2)	113·4 (2)

We associate the hopping mechanism with the layer structure in the crystal. Upon heating, the crystal absorbs energy and the perhydropyrene molecules move thermally within the layer. A stress is built up and released at 344·5 K, when the layers shift relative to each other from an intermediate stable state to another before melting, and the crystal jumps. In the cooling process the mechanism is the same, the perhydropyrene molecules in the intermediate stable high-temperature state move back to the original state, again accompanied with crystal jumping. This kind of phase transformation is well known in metallurgy where martensite shows a similar behaviour, thus the term 'martensitic phase transition' (Smallman, 1970).

We have tried to measure the diffraction data at temperatures above 344·5 K to determine the structure of the high-temperature phase. However, owing to rapid sublimation of the crystals, we could not carry out the experiments as the crystals disappeared before data could be collected. We were more successful in this respect with the mentioned *myo*-inositol derivative where structure determinations at both sides of one of the two phase transitions were carried out (Steiner, Hinrichs, Saenger & Gigg, 1988; Steiner, Hinrichs, Gigg & Saenger, 1991).

The authors acknowledge Professor G. Mann, Leipzig, for his generous gift of the title compound, Dr W. Hinrichs for assistance with X-ray diffraction data collection, and Professor J. D. Dunitz for pointing out the similarity with martensitic phase transition. JD thanks the Alexander von Humboldt Foundation for a research fellowship. This work was supported by Fonds der Chemischen Industrie.

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Acta Cryst. (1991). B**47**, 742–745

A Single-Crystal Neutron Diffraction Refinement of Benzamide at 15 and 123 K

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(*Received* 13 *September* 1990; *accepted* 13 *February* 1991)

Abstract

C_7H_7NO, $P2_1/c$ with $Z = 4$, cell dimensions at 15 K [123 K] are $a = 5{\cdot}529(1)$ [5·549(1)], $b = 5{\cdot}033(1)$ [5·033(1)], $c = 21{\cdot}343(3)$ [21·548(4)] Å, $\beta = 88{\cdot}73(1)$ [89·22(1)]°, $V = 593{\cdot}77(1)$ [601·74(1)] Å^3, $D_m = 1{\cdot}358$ [1·337] g cm^{-3}. 2364 [2377] symmetry-independent reflections were measured at the Brookhaven High Flux Reactor [$\lambda = 1{\cdot}0411(1)$ Å]. Structure refinement gave values of $R(F^2) = 0{\cdot}044$ [0·063]. A rigid-body thermal motion analysis was applied. The internal modes for the C—H and N—H bonds were calculated. The benzene ring has a small B_5^2 distortion, with benzene C—C bond lengths, corrected for thermal motion, ranging from 1·392(1) to 1·401(1) Å. The internal ring angles are 119·7(1) to 120·1(1)°. The amide bond lengths are C—C 1·498(1), C=O 1·246(1) and C—N 1·341(1) Å. Benzene C—H bond lengths range from 1·084(2) to 1·089(2) Å and N—H bond lengths are 1·013(2) and 1·022(2) Å. The plane of the amide group makes an angle of 25·2(1)° with the mean plane of the benzene ring.

Introduction

The crystal structure of benzamide was determined by single-crystal X-ray analysis at room temperature by Blake & Small (1972). We report a neutron diffraction refinement at 15 and 123 K to provide more precise molecular dimensions and for later use in a charge-density analysis based on X-ray data at those temperatures.

Experimental

Crystals of benzamide (Sigma Chemical Co.) were grown from benzene solution by slow evaporation. A crystal with dimensions 3·1 × 1·0 × 1·4 mm was selected for diffraction measurements. The data were collected at the Brookhaven High Flux Beam Reactor on the H6M four-circle diffractometer using a monochromated neutron beam obtained by reflection from Be(002) planes and calibrated against a reference KBr crystal ($a_0 = 6{\cdot}6000$ Å at 295 K). The temperature of the sample crystal was held within 0·5° of 15 and 123 K inside a closed-cycle helium refrigerator.‡ Measurements were made first at 15 K and then at 123 K. The lattice parameters, given in Table 1, were determined by least-squares fits to $\sin^2\theta$ vaues for 30 reflections with $52 < 2\theta < 57°$.

Table 1. *Crystal data for benzamide*

$C_6H_5CONH_2$; space group $P2_1/c$; $Z = 4$, molecular symmetry 1.

	Neutron data (λ = 1·0411 Å) (this work) 15 K	123 K	X-ray data (λ = 1·5418 Å) (Blake & Small, 1972) 295 K
a (Å)	5·529 (1)	5·549 (1)	5·607 (2)
b (Å)	5·033 (1)	5·033 (1)	5·046 (2)
c (Å)	21·343 (3)	21·548 (4)	22·053 (8)
β (°)	88·73 (1)	89·22 (1)	89·34
V (Å^3)	593·77 (1)	601·74 (1)	623·90
D_x (g cm^{-3})	1·355	1·337	1·288
μ_n (cm^{-1})	1·857		

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0108-7681/91/050742-04$03.00