

Fig. 2. A stereoview perpendicular to the *ab* plane.

BD₄ respectively in [Cu(phen)BH₄(tpp)] (Green, Kennard, Smith, Elcombe, Moore, James & White, 1984) to give the following corresponding angles and distances: B—Cu—P 120.3 (3), 116.7 (9)°; B—Cu—P—C(21) 31.6 (3), -36.6 (9)°; and Cu—B 2.28 (1), 2.29 (2) Å. These results suggest that the change in torsion angle in the two (II) examples is probably due to the steric hindrance of the bulkier BH₄ or BD₄ group.

The Cl atoms hydrogen bonded to O from one water molecule are also similarly bonded to water at a symmetry-related position down the *c* axis at *x* = 0 and *y* = 0.5 [Cl...O 3.25 (1), 3.30 (1) Å] (Fig. 2). This is comparable to the intramolecular Cl...O link of 3.109 (7) Å in aquatrifluorohydroxo[3,6-di(2-pyridyl)pyridazine]dicopper(II), (III) (Ghedini, deMunno, Denti, Lanfredi & Tiripicchio, 1982). The pyridine rings are planar but twisted with respect to each other about

the C(11)—C(14) bond [dihedral angle 5.7 (1)°, torsion angle N(1)—C(11)—C(14)—N(10) 7.8 (1)°] and this too is comparable to (III).

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Structural Studies of the System *trans*-Azobenzene/*trans*-Stilbene. II. A Reinvestigation of the Disorder in the Crystal Structure of *trans*-Stilbene, C₁₄H₁₂

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Abstract. *M_r* = 180.25, monoclinic, *P*2₁/*c*, *a* = 15.709 (3), *b* = 5.723 (1), *c* = 12.374 (2) Å, β = 111.90 (2)°, *V* = 1029.9 (2) Å³, *Z* = 4, *D_x* = 1.160 Mg m⁻³, λ(Mo *K*α) = 0.7107 Å, μ = 0.33 mm⁻¹, *F*(000) = 384, *T* = 295 K. A model in which the disorder at one of the two independent molecule sites was taken into account refined, using constraints and restraints, with 2276 observed diffractometer data to an *R* of 0.060. The nature of disorder and the degree of misorientation (13%) are very similar to those of *trans*-azobenzene [Bouwstra, Schouten & Kroon (1983). *Acta Cryst.* **C39**, 1121–1123].

Introduction. The crystal structure of *trans*-stilbene was determined by Robertson & Woodward (1937); the analysis was based on projection data. The molecular structure was frequently used for theoretical investigations and hence the availability of more accurate geometrical data became of interest. For that reason the structure has been redetermined: two structure refinements from different groups at room temperature (Finder, Newton & Allinger, 1974; Bernstein, 1975) and one at low temperature (113 K; Hoekstra, Meertens & Vos, 1975). From these investigations it appeared that one of the two independent

sites showed orientational disorder, albeit that the second orientation of the molecule is hardly present at 113 K. A similar kind of disorder in *trans*-azobenzene had already been suggested by Brown (1966).

Recently we prepared homogeneous mixed single crystals of *trans*-stilbene and *trans*-azobenzene with the zone-levelling technique (Kolkert, 1974). To solve the structure of these mixed single crystals we were in need of a more quantitative insight into the disorder in the structure of the pure substances. In Part I of this series we reported a reinvestigation of *trans*-azobenzene (Bouwstra, Schouten & Kroon, 1983) in which the disorder was taken into account. In this part the same model is applied to the structure refinement of *trans*-stilbene. In Part III the structure determination of the mixed crystals will be reported.

Experimental. Colourless block-shaped crystals of *trans*-stilbene, $0.3 \times 0.3 \times 0.3$ mm (m.p. 398.0 K), obtained by vacuum sublimation; sealed in capillary glass tube to avoid sublimation. Enraf-Nonius CAD-4 diffractometer, Zr-filtered Mo $K\alpha$ radiation. Lattice parameters refined by fitting to θ , φ , ω and κ settings of 24 reflections. Corresponding cell dimensions by Bernstein (1975): $a = 15.679$ (5), $b = 5.720$ (1), $c = 12.382$ (6) Å, $\beta = 111.96$ (3)°. 3186 unique reflections, $2\theta \leq 70^\circ$, hkl range: $h -25-22$, $k 0-9$, $l -19$, $\omega-2\theta$ scan, 002 reflection monitored periodically, decrease in intensity 8%, absorption ignored; 2276 reflections with $I > 2.5\sigma(I)$ used in subsequent structure refinement.

The molecule in the ordered position (referred to as molecule *A* at site *A*) and the molecule with the main-site occupancy in the disordered position (referred to as molecule *B1* at site *B*) were located with *MULTAN* (Germain, Main & Woolfson, 1971). A difference electron density map was calculated, but in contrast with the structure determination of *trans*-azobenzene (Bouwstra *et al.*, 1983) this map did not reveal the second molecule in the disordered position. Therefore one cycle of least-squares refinement was performed and again a difference synthesis was calculated: six C atoms of the second molecule in the disordered position (referred to as molecule *B2*) could clearly be located. The five already located C atoms belonging to the benzene ring were fitted to a regular hexagon.

The least-squares refinement based on *F* was carried out with the following model. The benzene rings at molecules *B1* and *B2* were refined as rigid groups; slack constraints (Waser, 1963) were applied to their *exo*-ring distances. These were restrained to values found for molecule *A* and are given in Table 2. The H atoms, introduced for molecules *A* and *B1*, were set at a distance of 1 Å from their carrier atoms, assuming sp^2 hybridization. The fractional coordinates of these H atoms were not refined but supposed to 'ride on' their

carrier atoms. The occupancy ratio of the molecules at site *B* was initially set at 0.85:0.15, in view of energy calculations on *trans*-stilbene (Bernstein & Mirsky, 1978) which indicated that the degree of misorientation should not exceed 20%. The atoms of molecule *B2* were refined with one overall isotropic temperature factor.

After isotropic block refinement the occupancy parameters were fixed to avoid correlation effects during the succeeding refinements. The final occupancy ratio is 0.88 (1):0.12 (1). During the anisotropic full-matrix refinement the *R* dropped to a value of 0.060 ($R_w = 0.079$, $S = 0.3$; 120 variables). The weighting scheme applied is $[\sigma^2(F) + 0.0078 F^2]^{-1}$. Using our intensities and Bernstein's model (with 175 variables) the *R* reduced only to a value of 0.071, this justifying the introduction of the model for disordering.

Final difference synthesis essentially featureless: $|\Delta\rho| \leq 0.26 e \text{ \AA}^{-3}$; $(\Delta/\sigma)_{\text{ave}} = 0.59$, $(\Delta/\sigma)_{\text{max}} = 2.2$. Scattering factors for N and C from Cromer & Mann (1968), for H the *f* curve of Stewart, Davidson & Simpson (1965). All calculations carried out with *SHELX76* (Sheldrick, 1976).

Discussion. Final coordinates and equivalent isotropic temperature factors are collected in Table 1.*

* Lists of structure factors, H-atom coordinates and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38973 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Positional ($\times 10^4$) and equivalent isotropic thermal ($\text{\AA}^2 \times 10^4$) parameters with their *e.s.d.*'s in parentheses

Molecule	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}	U_{eq}
					(Bernstein, 1975)
$U_{\text{eq}} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$					
Molecule <i>A</i>					
C(1)	4768 (1)	955 (3)	5021 (1)	467 (4)	493
C(2)	4237 (1)	1332 (3)	5765 (1)	426 (4)	436
C(3)	3730 (1)	3380 (3)	5635 (1)	518 (5)	537
C(4)	3203 (1)	3810 (3)	6294 (2)	595 (5)	592
C(5)	3182 (1)	2188 (3)	7110 (2)	584 (5)	594
C(6)	3692 (1)	158 (3)	7267 (1)	562 (5)	571
C(7)	4217 (1)	-268 (3)	6608 (1)	474 (4)	496
Molecule <i>B1</i>					
C(8)	9686 (1)	753 (3)	9679 (1)	530 (5)	680
C(9)	9171 (1)	640 (2)	8412 (1)	478 (5)	559
C(10)	9264 (1)	-1225 (2)	7738 (1)	573 (6)	667
C(11)	8765 (1)	-1249 (2)	6540 (1)	626 (7)	638
C(12)	8172 (1)	591 (2)	6016 (1)	589 (6)	657
C(13)	8079 (1)	2456 (2)	6690 (1)	629 (7)	651
C(14)	8579 (1)	2480 (2)	7888 (1)	584 (6)	695
Molecule <i>B2</i>					
C(15)	9900 (6)	-685 (10)	9535 (3)	466 (10)	
C(16)	9286 (6)	-101 (17)	8340 (2)	466 (10)	
C(17)	9169 (6)	-1548 (17)	7388 (2)	466 (10)	
C(18)	8580 (6)	-879 (17)	6276 (2)	466 (10)	
C(19)	8108 (6)	1237 (17)	6116 (2)	466 (10)	
C(20)	8225 (6)	2684 (17)	7068 (2)	466 (10)	
C(21)	8813 (6)	2015 (17)	8180 (2)	466 (10)	

A projection along the b axis, including both molecules at site B , is given in Fig. 1. In this projection molecule A and molecule $B1$ are nearly interchangeable when the structure is rotated by 180° about the $[201]$ axis, which is approximately perpendicular to the c axis. In Fig. 2(a) both molecules in the disordered site are drawn. From this figure it is clear that the positions of the molecules are very similar. As in azobenzene the molecules are nearly related by a twofold axis: a rotation by 180° about approximately the direction of the longest axis results in a mean positional deviation of 0.11 \AA . The distance $\text{H}(8)\text{--C}(15^{\text{II}})$ and angle $\text{H}(8)\text{--C}(15^{\text{II}})\text{--C}(16^{\text{II}})$ are 1.15 \AA and 132° respectively, which implies that the positions of $\text{H}(8)$ and $\text{H}(15^{\text{II}})$ [carrier atom $\text{C}(15^{\text{II}})$] are almost the same.

From Table 1 it can be inferred that the thermal parameters at site B are lower than those found by Bernstein (1975), although the thermal motion at site A is still smaller than at site B , which is probably due to more available space at site B (*cf.* Brown, 1966). The

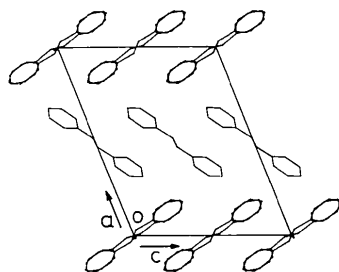


Fig. 1. Projection of the structure along b , showing the disorder at site B .

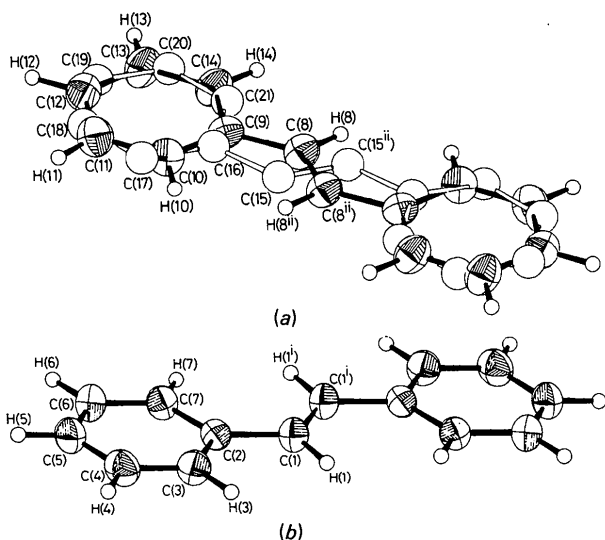


Fig. 2. (a) A composite view of the disordered molecules at site B with 50% probability plots for thermal ellipsoids of molecule $B1$. (b) View of the molecule at site A with 50% probability plots for thermal ellipsoids.

Table 2. Bond distances (\AA) and bond angles ($^\circ$) in stilbene with occasional restraints imposed during the refinement

In the third column values found by Bernstein (1975) are given. Roman numerals indicate symmetry-related units according to the following code: (i) $1 - x, -y, 1 - z$; (ii) $2 - x, -y, 2 - z$.

	Present work	Bernstein (1975)
Molecule A		
$\text{C}(1)\text{--C}(1^{\text{I}})$	1.326 (2)	1.313
$\text{C}(1)\text{--C}(2)$	1.471 (2)	1.471
$\text{C}(2)\text{--C}(3)$	1.392 (2)	1.388
$\text{C}(3)\text{--C}(4)$	1.384 (3)	1.381
$\text{C}(4)\text{--C}(5)$	1.381 (3)	1.375
$\text{C}(5)\text{--C}(6)$	1.383 (2)	1.381
$\text{C}(6)\text{--C}(7)$	1.381 (2)	1.382
$\text{C}(2)\text{--C}(7)$	1.397 (2)	1.392
$\text{C}(1^{\text{I}})\text{--C}(1)\text{--C}(2)$	126.4 (1)	127.0
$\text{C}(1)\text{--C}(2)\text{--C}(3)$	119.0 (1)	119.2
$\text{C}(2)\text{--C}(3)\text{--C}(4)$	121.6 (1)	121.6
$\text{C}(3)\text{--C}(4)\text{--C}(5)$	119.6 (2)	120.0
$\text{C}(4)\text{--C}(5)\text{--C}(6)$	119.8 (2)	119.4
$\text{C}(5)\text{--C}(6)\text{--C}(7)$	120.5 (2)	120.6
$\text{C}(6)\text{--C}(7)\text{--C}(2)$	120.7 (2)	120.6
$\text{C}(7)\text{--C}(2)\text{--C}(1)$	123.2 (1)	123.1
$\text{C}(3)\text{--C}(2)\text{--C}(7)$	117.8 (1)	117.6
Molecules $B1$ and $B2^*$		
$\text{C}(8)\text{--C}(8^{\text{II}})$	1.328 (2)	1.228
$\text{C}(15)\text{--C}(15^{\text{II}})$	1.330 (8)	
Restraint	1.330 (1)	
$\text{C}(8)\text{--C}(9)$	1.473 (2)	1.484
$\text{C}(15)\text{--C}(16)$	1.471 (9)	
Restraint	1.471 (1)	
$\text{C}(8^{\text{II}})\text{--C}(8)\text{--C}(9)$	126.8 (1)	127.0
$\text{C}(15^{\text{II}})\text{--C}(15)\text{--C}(16)$	126.2 (7)	
Restraint	126.1	
$\text{C}(8)\text{--C}(9)\text{--C}(14)$	117.9 (1)	117.1
$\text{C}(15)\text{--C}(16)\text{--C}(21)$	117.0 (6)	
$\text{C}(8)\text{--C}(9)\text{--C}(10)$	122.1 (1)	125.2
$\text{C}(15)\text{--C}(16)\text{--C}(17)$	123.0 (8)	

* Intra-ring bond lengths are 1.395 \AA ; intra-ring bond angles are 120° .

Table 3. Selected torsion angles ($^\circ$) in stilbene

$\text{C}(1^{\text{I}})\text{--C}(1)\text{--C}(2)\text{--C}(3)$	-175.0 (2)
$\text{C}(1^{\text{I}})\text{--C}(1)\text{--C}(2)\text{--C}(7)$	5.3 (2)
$\text{C}(8^{\text{II}})\text{--C}(8)\text{--C}(9)\text{--C}(10)$	3.6 (2)
$\text{C}(8^{\text{II}})\text{--C}(8)\text{--C}(9)\text{--C}(14)$	-176.1 (2)
$\text{C}(15^{\text{II}})\text{--C}(15)\text{--C}(16)\text{--C}(17)$	174.3 (8)
$\text{C}(15^{\text{II}})\text{--C}(15)\text{--C}(16)\text{--C}(21)$	-5.3 (12)

established degree of disorder of 12% corresponds with a decrease in free energy of 0.46 kJ mol^{-1} due to the ideal entropy of mixing at room temperature. This value has to be compared with 0.59 kJ mol^{-1} which has been calculated as the increase in lattice energy caused by a partial disordering of 20% (Bernstein & Mirsky, 1978). A view of molecule A along with the atomic-numbering scheme is shown in Fig. 2(b). Bond distances and bond angles are given in Table 2. In Table 3 some relevant torsion angles are given. As was already observed by Finder *et al.* (1974) the molecules at both independent sites have a nearly planar conformation. There are no intermolecular distances which are significantly less than the van der Waals radii.

Finally it is noteworthy that *trans*-azobenzene and *trans*-stilbene are not only isostructural and have almost the same packing coefficients (Kitaigorodsky, 1973), which are 0.75 and 0.74 respectively, but also show the same kind and degree of disorder. With this similarity in mind we can imagine that these molecules form a continuous series of mixed crystals.

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15,30-Dihydroxy-12,27-dimethyl-5,20-dioxa-2,8,17,23-tetrathia[9.9]metacyclophane, C₂₆H₃₆O₄S₄

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Abstract. $M_r = 540.83$, orthorhombic, $Pbca$, $a = 28.25$ (1), $b = 9.14$ (1), $c = 10.27$ (1) Å, $V = 2652$ (4) Å³, $Z = 4$, $D_m = 1.34$, $D_x = 1.35$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 3.40$ cm⁻¹, $F(000) = 1152$, $T = 293$ K. Final $R = 0.092$ for 1248 observed reflections. The molecule is a centrosymmetric 24-membered metacyclophane macrocycle. The intraannular hydroxyl groups are hydrogen-bonded to oxa ring atoms leading to the formation of two internal eight-membered rings; moreover, they are involved in transannular non-bonding interactions.

Introduction. Polycondensation in benzyl alcohol of 2,6-bis[(dimethylamino)methyl]-4-methylphenol with 2,2'-oxydiethanedithiol gives both a linear polymer and a macrocycle, which were characterized by several techniques (Costa Bizzarri, Della Casa, Ferruti, Ghedini, Pilati & Scapini, 1983); molecular-weight determination and a mass spectrum suggested a 12-membered ring for the macrocycle, while ¹H NMR spectra seem to indicate the presence of a larger ring. In order to elucidate this problem single-crystal X-ray analysis was undertaken.

Experimental. Crystals, in form of colourless prisms, obtained by evaporating a toluene solution for several days, and supplied by Costa Bizzarri

et al. D_m measured by flotation. Crystal of dimensions 0.21 × 0.24 × 0.35 mm used for data collection on an automatic Siemens AED diffractometer using Zr-filtered Mo $K\alpha$ radiation. Accurate cell dimensions and orientation matrix obtained from least-squares fit of θ , χ , φ values of 14 reflections in range $15 \leq \theta \leq 18^\circ$, measured by use of a narrow counter aperture. 2318 reflections up to $2\theta = 50^\circ$ (hkl range: 0–33, 0–10, 0–12) measured by θ – 2θ scan technique; intensities of three standard reflections, 512, $\bar{5}12$, $\bar{5}\bar{1}\bar{2}$, measured at 4 h intervals, no significant variation throughout data collection. Systematic absences: $Ok\bar{l}$, $k = 2n + 1$; $h0l$, $l = 2n + 1$; $hk0$, $h = 2n + 1$ consistent with space group $Pbca$ (No. 61). Intensities corrected for Lorentz and polarization factors. Structure solved by *MULTAN80* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980) and refined by full-matrix least squares using 1248 reflections having $I \geq 3\sigma(I)$; refined quantity $\sum w\Delta F^2$, where $w = 1/\sigma^2$. A difference Fourier synthesis in final stages of refinement clearly indicated positions of all H atoms, except those of methyl group; residual electron density within -0.30 and 0.32 e Å⁻³. H contribution included and held fixed in final least-squares cycles, where S atoms refined anisotropically; $R = 0.092$, $wR = 0.086$, $S = 3.3$; max. $\Delta/\sigma = 0.19$. *SHELXTL* used throughout (Sheldrick, 1981). Atomic scattering factors from *International Tables for X-ray Crystallography* (1974).