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 C1...O link of 3.109 (7) Å in aquatrichlorohydroxo[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).

The authors wish to thank the University of Queensland for support, the University of Western Australia for the use of data-collection facilities and the Queensland Institute of Technology for leave to work on this project (GS).

References

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-leveling technique (Kolker, 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 x 0.3 x 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 Kα 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, β = 111.96 (3)°. 3186 unique reflections, 2θ ≤ 70°, hkl range: h = -25-22, k = 0-9, l = 0-19, ω-2θ scan, 002 reflection monitored periodically, decrease in intensity 8%, absorption ignored; 2276 reflections with I > 2.5σ(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 sp² 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 (Rw = 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: $|\Delta f| \leq 0.26$ e Å$^{-3}$; $(\Delta f)_{\text{avg}} = 0.59$, $(\Delta f)_{\text{max}} = 2.2$. 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 ($\AA^2 \times 10^4$) parameters with their e.s.d.'s in parentheses

<table>
<thead>
<tr>
<th>Molecule</th>
<th>$x$</th>
<th>$y$</th>
<th>$z$</th>
<th>$U_{eq}$</th>
<th>$U_{eq}$ (Bernstein, 1975)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(1)</td>
<td>4768 (1)</td>
<td>955 (3)</td>
<td>5021 (1)</td>
<td>467 (4)</td>
<td>493</td>
</tr>
<tr>
<td>C(2)</td>
<td>4237 (1)</td>
<td>1232 (3)</td>
<td>5765 (1)</td>
<td>426 (4)</td>
<td>436</td>
</tr>
<tr>
<td>C(3)</td>
<td>3730 (1)</td>
<td>3380 (3)</td>
<td>5635 (1)</td>
<td>518 (5)</td>
<td>537</td>
</tr>
<tr>
<td>C(4)</td>
<td>3203 (1)</td>
<td>3810 (3)</td>
<td>6294 (2)</td>
<td>595 (5)</td>
<td>592</td>
</tr>
<tr>
<td>C(5)</td>
<td>3182 (1)</td>
<td>2188 (3)</td>
<td>7110 (2)</td>
<td>584 (5)</td>
<td>594</td>
</tr>
<tr>
<td>C(6)</td>
<td>3692 (1)</td>
<td>158 (3)</td>
<td>7267 (1)</td>
<td>562 (5)</td>
<td>571</td>
</tr>
<tr>
<td>C(7)</td>
<td>4217 (1)</td>
<td>-268 (3)</td>
<td>6608 (1)</td>
<td>474 (4)</td>
<td>496</td>
</tr>
<tr>
<td>B1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(8)</td>
<td>9686 (1)</td>
<td>753 (3)</td>
<td>9679 (1)</td>
<td>530 (5)</td>
<td>680</td>
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<tr>
<td>C(9)</td>
<td>9171 (1)</td>
<td>640 (2)</td>
<td>8412 (1)</td>
<td>478 (5)</td>
<td>559</td>
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<tr>
<td>C(10)</td>
<td>9264 (1)</td>
<td>-1225 (2)</td>
<td>7738 (1)</td>
<td>573 (6)</td>
<td>667</td>
</tr>
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<td>C(11)</td>
<td>8765 (1)</td>
<td>-1249 (2)</td>
<td>6540 (1)</td>
<td>626 (7)</td>
<td>638</td>
</tr>
<tr>
<td>C(12)</td>
<td>8172 (1)</td>
<td>591 (2)</td>
<td>6016 (1)</td>
<td>589 (6)</td>
<td>657</td>
</tr>
<tr>
<td>C(13)</td>
<td>8079 (1)</td>
<td>2456 (2)</td>
<td>6990 (1)</td>
<td>629 (7)</td>
<td>651</td>
</tr>
<tr>
<td>C(14)</td>
<td>8579 (1)</td>
<td>2480 (2)</td>
<td>7888 (1)</td>
<td>584 (6)</td>
<td>695</td>
</tr>
<tr>
<td>B2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(15)</td>
<td>9900 (6)</td>
<td>-685 (10)</td>
<td>9535 (3)</td>
<td>466 (10)</td>
<td></td>
</tr>
<tr>
<td>C(16)</td>
<td>9286 (6)</td>
<td>-101 (17)</td>
<td>8340 (2)</td>
<td>466 (10)</td>
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</tr>
<tr>
<td>C(17)</td>
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<td>-1548 (17)</td>
<td>7388 (2)</td>
<td>466 (10)</td>
<td></td>
</tr>
<tr>
<td>C(18)</td>
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<td>-879 (17)</td>
<td>6276 (2)</td>
<td>466 (10)</td>
<td></td>
</tr>
<tr>
<td>C(19)</td>
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<td>1237 (17)</td>
<td>6116 (2)</td>
<td>466 (10)</td>
<td></td>
</tr>
<tr>
<td>C(20)</td>
<td>8225 (6)</td>
<td>2684 (17)</td>
<td>7068 (2)</td>
<td>466 (10)</td>
<td></td>
</tr>
<tr>
<td>C(21)</td>
<td>8813 (6)</td>
<td>2015 (17)</td>
<td>8180 (2)</td>
<td>466 (10)</td>
<td></td>
</tr>
</tbody>
</table>
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 Å. The distance \( H(8)--C(15) \) and angle \( H(8)--C(15)--C(16) \) are 1.15 Å and 132° respectively, which implies that the positions of \( H(8) \) and \( H(15) \) are almost the same.

From Table I 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 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).

Table 2. Bond distances (Å) and bond angles (°) in stilbene with occasional restraints imposed during the refinement

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Present work</th>
<th>Bernstein (1975)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( A )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( C(1)--C(1') )</td>
<td>1.326 (2)</td>
<td>1.313</td>
</tr>
<tr>
<td>( C(2)--C(2) )</td>
<td>1.397 (2)</td>
<td>1.388</td>
</tr>
<tr>
<td>( C(3)--C(3') )</td>
<td>1.384 (3)</td>
<td>1.381</td>
</tr>
<tr>
<td>( C(4)--C(4') )</td>
<td>1.381 (3)</td>
<td>1.375</td>
</tr>
<tr>
<td>( C(5)--C(5') )</td>
<td>1.383 (2)</td>
<td>1.381</td>
</tr>
<tr>
<td>( C(6)--C(6') )</td>
<td>1.381 (2)</td>
<td>1.382</td>
</tr>
<tr>
<td>( C(7)--C(7') )</td>
<td>1.397 (2)</td>
<td>1.392</td>
</tr>
<tr>
<td>( C(8)--C(8') )</td>
<td>1.328 (2)</td>
<td>1.228</td>
</tr>
<tr>
<td>( C(9)--C(9') )</td>
<td>1.473 (2)</td>
<td>1.484</td>
</tr>
<tr>
<td>( C(10)--C(10') )</td>
<td>1.471 (9)</td>
<td>1.471 (1)</td>
</tr>
<tr>
<td>( C(11)--C(11') )</td>
<td>1.471 (9)</td>
<td>1.471 (1)</td>
</tr>
<tr>
<td>( C(12)--C(12') )</td>
<td>1.471 (1)</td>
<td>1.471 (1)</td>
</tr>
</tbody>
</table>

Table 3. Selected torsion angles (°) in stilbene

<table>
<thead>
<tr>
<th>Torsion Angle</th>
<th>Present work</th>
</tr>
</thead>
<tbody>
<tr>
<td>( C(1')--C(1)--C(2)--C(3) )</td>
<td>-175.0 (2)</td>
</tr>
<tr>
<td>( C(1')--C(1)--C(2)--C(7) )</td>
<td>5.3 (2)</td>
</tr>
<tr>
<td>( C(8')--C(8)--C(9)--C(10) )</td>
<td>3.6 (2)</td>
</tr>
<tr>
<td>( C(8')--C(8)--C(9)--C(14) )</td>
<td>-176.1 (2)</td>
</tr>
<tr>
<td>( C(15')--C(15)--C(16)--C(17) )</td>
<td>174.3 (8)</td>
</tr>
<tr>
<td>( C(15')--C(15)--C(16)--C(21) )</td>
<td>-5.3 (12)</td>
</tr>
</tbody>
</table>

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

We thank Drs A. J. M. Duijzenberg for collecting the intensity data.

References


15,30-Dihydroxy-12,27-dimethyl-5,20-dioxa-2,8,17,23-tetrathia[9.9]metacyclophane, C_{26}H_{36}O_{48}S_{4}

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(Rceived 21 July 1983; accepted 24 October 1983)

Abstract. $M_f=540.83$, orthorhombic, $Pbca$, $a=28.25$ (1), $b=9.14$ (1), $c=10.27$ (1), $V=2652$ (4) Å$^3$, $Z=4$, $D_m=1.34$, $D_x=1.35$ g cm$^{-3}$, $\lambda$(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 $^1$H 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 tolulene solution for several days, and supplied by Costa Bizzarri et al. $D_m$ measured by flotation. Crystal of dimensions 0.21 x 0.24 x 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 $\theta$, $\chi$, $\phi$ values of 14 reflections in range $15^\circ \leq \theta \leq 18^\circ$, 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 $\omega-\theta$ scan technique; intensities of three standard reflections, 512, 512, 512, measured at 4 h intervals, no significant variation throughout data collection. Systematic absences: $0kl$, $k=2n+1$; $h0l$, $l=2n+1$; $hk0$, $h=2n+1$ 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 $\sum wAF^2$, 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).