Acta Cryst. (1985). C**41**, 420–426

Structural Studies of the System *trans*-Stilbene/*trans*-Azobenzene. III. The Structures of Three Mixed Crystals of *trans*-Azobenzene/*trans*-Stilbene; Determinations by X-ray and Neutron Diffraction

By J. A. Bouwstra, A. Schouten and J. Kroon

Laboratoria voor Chemische Thermodynamica en Kristal- en Structuurchemie, Rijksuniversiteit, Padualaan 8, *Utrecht, The Netherlands*

and R. B. Helmholdt

Netherlands Energy Research Foundation, ECN, PO Box 1, 1755 *ZG Petten, The Netherlands*

(*Received* 25 *July* 1984; *accepted* 19 *October* 1984)

Abstract. $(C_{14}H_{12})_X(C_{12}H_{10}N_2)_{(1-X)}$, monoclinic, $P2_1/c$, $Z = 4$, $T = 295$ K. (I) $X = 0{\cdot}26$: $M_r = 181{\cdot}71$, $a = 15{\cdot}306$ (2), $b = 5{\cdot}7716$ (4), $c = 12{\cdot}230$ (2) Å, $\beta = 112{\cdot}04$ (1)°, $V = 1001{\cdot}5$ (4) Å^3, $D_x = 1{\cdot}205$ Mg m^{-3}, λ(Cu $K\alpha$) = 1·5418 Å, $\mu = 0{\cdot}47$ mm^{-1}, $F(000) = 384$, final $R = 0{\cdot}056$ for 1706 unique X-ray data. (II) $X = 0{\cdot}56$: $M_r = 181{\cdot}12$, $a = 15{\cdot}481$ (3), $b = 5{\cdot}749$ (1), $c = 12{\cdot}300$ (2) Å, $\beta = 111{\cdot}98$ (1)°, $V = 1015{\cdot}1$ (5) Å^3, $D_x = 1{\cdot}185$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 0{\cdot}36$ mm^{-1}, $F(000) = 384$, final $R = 0{\cdot}051$ for 1586 X-ray data. (III) $X = 0{\cdot}46$: $M_r = 181{\cdot}32$, $a = 15{\cdot}409$ (5), $b = 5{\cdot}759$ (1), $c = 12{\cdot}284$ (4) Å, $\beta = 111{\cdot}97$ (3)°, $V = 1010{\cdot}9$ (7) Å^3, $D_x = 1{\cdot}191$ Mg m^{-3}, $\lambda = 1{\cdot}304$ Å, $\mu = 0{\cdot}186$ mm^{-1}, $F(000) = 21{\cdot}36$, final $R = 0{\cdot}082$ for 910 neutron reflection data. (IV) $X = 0{\cdot}69$: $M_r = 181{\cdot}72$, $a = 15{\cdot}548$ (2), $b = 5{\cdot}7388$ (4), $c = 12{\cdot}333$ (2) Å, $\beta = 111{\cdot}92$ (2)°, $V = 1020{\cdot}9$ (5) Å^3, $D_x = 1{\cdot}183$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å; no structure determination. The mixed crystals not only exhibit substitutional disorder but both molecules, *trans*-azobenzene and *trans*-stilbene, also show configurational disorder at one of the two independent sites with symmetry $\bar{1}$. The structure refinements, in which both kinds of disorder were taken into account, were performed with constraints and restraints. The *trans*-stilbene molecules show a slight preference for substitution at the disordered sites. This preference can be understood by geometrical considerations.

Introduction. In the course of thermodynamical research into the system *trans*-azobenzene/*trans*-stilbene we have carried out structural studies of some mixed crystals by X-ray and neutron diffraction.

The crystal-structure determinations of the pure substances *trans*-azobenzene (Brown, 1966) and *trans*-stilbene (Hoekstra, Meertens & Vos, 1975; Finder, Newton & Allinger, 1974; Bernstein, 1975) led to the suggestion that both *trans*-stilbene and *trans*-azobenzene show configurational disorder at one of the two independent sites. To solve the structures of the mixed crystals we were in need of a better determination of the mentioned disorder. In part I (Bouwstra, Schouten & Kroon, 1983) of this series the structure of *trans*-azobenzene has been redetermined using a model in which the disorder was taken into account. In part II (Bouwstra, Schouten & Kroon, 1984) the same model was applied to the structure refinement of *trans*-stilbene. It appeared that both structures show the same kind of disorder and that the molecules at the disordered site are approximately related by a twofold axis. 17% and 12% of the molecules *trans*-azobenzene and *trans*-stilbene were misoriented. From this it follows that *trans*-azobenzene and *trans*-stilbene are not only isostructural but also show the same kind and approximately the same degree of disorder. Moreover the two structures have almost the same packing coefficients (Kitaigorodskii, 1973), which are 0·74 and 0·75 for *trans*-azobenzene and *trans*-stilbene respectively. Following Kitaigorodskii these molecules fulfil all conditions to form mixed crystals.

From the literature only a few structural studies on organic mixed crystals are known. In the early seventies Frank, Myasnikova & Kitaigorodskii (1971) analyzed solid solutions of the system *trans*-stilbene/diphenylmercury. They found that in the case of solid solutions containing 8% diphenylmercury these molecules were preferentially substituted at one of the two independent sites. At the same time Frank *et al.* performed energy calculations on this system. They used a model in which diphenylmercury was infinitely diluted. These calculations confirmed the X-ray studies and indicated that diphenylmercury substituted at one site leads to a lower lattice energy than diphenylmercury substituted at the other site.

The preparation of homogeneous mixed crystalline material has always been a great problem: crystal-

0108-2701/85/030420-07$01.50

lization from the melt often leads to inhomogeneities in the solid state due to the low diffusion rate in the solid material. In our group this problem has been solved by the introduction of the zone-levelling technique. Recently we prepared homogeneous mixed single crystals of the system *trans*-azobenzene/*trans*-stilbene.

The crystal structures of these mixed crystals are much more complicated than those of the pure components. At both independent sites, *i.e.* the ordered site (denoted as site *A*) and the disordered site (denoted as site *B*), *trans*-azobenzene molecules as well as *trans*-stilbene molecules can be substituted. This means that site *B* contains four crystallographically different molecules.

We were particularly interested in the distributions of the stilbene molecules between site *A* and site *B*. To determine the occupancy of stilbene molecules at both sites we first undertook an X-ray analysis of two mixed crystals containing 26% ($X = 0{\cdot}26$) and 56% ($X = 0{\cdot}56$) stilbene. However, it appeared that the positions of *trans*-azobenzene and *trans*-stilbene molecules are very similar. For that reason the percentage stilbene present at site *A* and site *B* could not be determined very accurately. Because the H atoms attached to the ethene bond of stilbene are the only atoms that are not closely positioned to azobenzene we decided to use them as probes and deemed it useful to study a mixed crystal ($X = 0{\cdot}46$) by neutron diffraction.

Experimental. Lattice parameters of three mixed crystals (composition: $X = 0{\cdot}26$, $X = 0{\cdot}56$ and $X = 0{\cdot}69$) refined by fitting to θ, φ, ω and κ settings of 24 reflections in θ range 7 to 9° using Zr-filtered Mo $K\alpha$ radiation. Lattice parameters of a fourth crystal ($X = 0{\cdot}46$) refined by fitting 2θ settings of 13 reflections in θ range 40 to 50° using neutrons with a wavelength of 1·304 Å. Data collection and structure refinement of three mixed crystals, all prepared by the zone-levelling technique, are given separately.

(I) $X = 0{\cdot}26$

Red block-shaped crystals, 0·28 × 0·30 × 0·25 mm. Enraf–Nonius CAD-4 diffractometer, Zr-filtered Cu $K\alpha$ radiation. 7356 reflections measured ($2\theta < 70°$, *hkl* range: h −15–14; k −7–7; l −18–18), 1869 unique reflections ($R_{\rm int} = 0{\cdot}041$), 1706 reflections with $I > 2{\cdot}5\sigma(I)$ considered observed and included in the refinement. 4 standard reflections measured every 110 reflections; decrease of intensity caused by sublimation was less than 30%; corrections for average change in intensity of reference reflections. Absorption correction ignored. The crystal structure of the mixed crystals is rather complicated (see above). Site *A* ($\frac{1}{2}$,0,$\frac{1}{2}$) is filled with *trans*-stilbene and *trans*-azobenzene (referred to as *A*1 and *A*2 respectively). At site *B* (0,0,0) four crystallographically different molecules have to be considered: *trans*-azobenzene and *trans*-stilbene, both molecules of which can adopt two orientations (see Fig. 1). We calculated the initial positions of the molecules from the structures of the pure components, leaving the geometry of the molecules intact. Least-squares refinement based on *F* was carried out using the following model. The benzene rings of the molecules at site *A* and the benzene rings of both *trans*-azobenzene and *trans*-stilbene with the main site occupancy at site *B* (referred to as *B*1 and *B*3 respectively) were refined as rigid bodies. Slack constraints (Waser, 1963) were applied to all *exo*-ring distances of these molecules. Not the whole molecule was treated as a rigid body because of our interest in the torsion angles in the central part of the molecule. *trans*-Azobenzene and *trans*-stilbene with the minor site occupancies at site *B* (referred to as *B*2 and *B*4) were fixed in space in view of the low occupancy values. The atoms at approximately the same position were refined with common temperature factors. Moreover, the occupancy ratios of the two orientations of *trans*-azobenzene (83:17) and *trans*-stilbene (88:12) were put equal to those obtained for the pure substances and were fixed during the refinement. Finally the distribution of stilbene molecules over site *A* and site *B* was refined keeping the sum of the occupancy values at both sites equal to 1. In this way the occupancy values are all governed by one variable: X', which stands for the fraction of the total amount stilbene present at site *A*. A scheme of the occupancy values is given in Fig. 1.

The initial *R* was 0·15. During the isotropic least-squares block refinement, which was carried out with a damping factor (Mackay, 1977), it appeared that the distribution of stilbene molecules over the two sites could not be refined probably due to correlation effects between occupancy factors and temperature factors. Therefore we repeated the isotropic refinement with several values of X'. This yielded a smooth variation in the *R* value as a function of X' as can be inferred from Fig. 2(*a*). The lowest *R* was obtained for $X' = 0{\cdot}30$; corresponding occupancy values are given in Table 1.

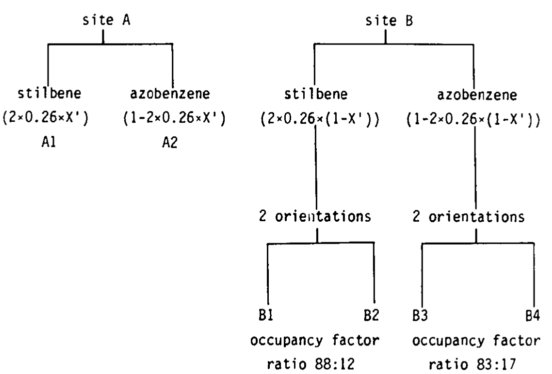

Fig. 1. Mixed crystal *trans*-azobenzene/*trans*-stilbene ($X = 0{\cdot}26$); example of the scheme of occupancy factors expressed in X'.

After the isotropic refinement H atoms were introduced for molecules $A1$, $A2$, $B1$ and $B3$. To allow for bond shortening these atoms were placed at a distance 1 Å from their carrier atoms assuming sp^2 hybridization. The positional parameters of the H atoms were not refined but these atoms 'ride' on their carrier atoms. During the anisotropic refinement the occupancy values corresponding to the lowest R index were used.

After the subsequent anisotropic refinement R dropped to a value of 0·06. Then the damping factor was removed and the anisotropic thermal parameters of molecules $A1$, $B1$, $B2$ and $B4$ with minor occupancy were replaced by the corresponding U_{eq}, otherwise no convergence could be achieved. The final anisotropic block refinement (with 121 variables, each block containing one molecule) resulted in an R of 0·056 ($S = 0·44$); mean Δ/σ and max. Δ/σ were 0·29 and 1·19 respectively. Min. trough and max. peak in final difference Fourier map are −0·21 and 0·23 e Å^{-3}. The positional parameters together with the temperature factors are given in Table 1.*

(II) $X = 0·56$

Red block-shaped crystal (0·20 × 0·25 × 0·25 mm), placed in a capillary glass tube to avoid sublimation, which was observed during data collection in case (I). 2762 unique reflections ($2\theta < 70°$, hkl range: h −24–24; k 0–9; l 0–19), 1586 reflections with $I > 2·5\sigma(I)$ considered observed and included in the refinement. 4 standard reflections measured every 100 reflections; drop of intensity less than 3%. Absorption correction ignored. The initial positions of the molecules were calculated using the structures of the pure components, leaving the geometry of the molecules intact. The refinement was performed with the same model as that applied to the structure of the mixed crystal with $X = 0·26$. Again the distribution of stilbene between the two independent sites could not be refined due to correlation effects. For that reason the isotropic refinement, which was carried out with a damping factor, was repeated with five values for X' (see Fig. 2*b*). In this case the lowest R value was obtained for $X' = 0·39$. At this stage of refinement the H atoms were introduced. The occupancy values corresponding to the lowest R value were used and fixed during the subsequent refinement. Then the anisotropic temperature parameters of the atoms belonging to molecules $A1$, $B2$, $B3$ and $B4$ were replaced by their corresponding U_{eq} parameters and the damping factor was removed. During the succeeding block refinement (with 121 variables, each block containing one molecule) R reduced to a value of 0·051 ($S = 0·57$). The final difference map was essentially featureless: min. trough −0·15 and max. peak 0·17 e Å^{-3}. Mean Δ/σ and max. Δ/σ were 0·15 and 0·92 respectively. Final coordinates and temperature factors are collected in Table 1. For the structure determinations of (I) and (II) the scattering factors for N and C were taken from Cromer & Mann (1968); for H the curve of Stewart, Davidson & Simpson (1965) was applied.

(III) $X = 0·46$

A red irregularly shaped crystal, volume about 10 mm^3, was coated with Krylon to avoid sublimation. The neutron data were collected on a four-circle diffractometer at the HFR reactor at Petten. Neutrons with a wavelength of 1·304 Å were obtained after diffraction from the 220 planes of the Cu crystals of a double monochromator. Reflections were measured in the ω–2θ step-scan mode (0·0625° step^{-1}) at room temperature. 1753 unique reflections ($2\theta_{max} = 100°$, hkl range: h −15–14; k 0–4; l 0–12), 910 of which with $F > 4\sigma(F)$ used in least-squares refinement. 2 standard reflections measured every 50 reflections; fluctuations not greater than 2%. Initial positions of the molecules calculated from the structures of the pure substances. The refinement was carried out with the same model as was used in cases (I) and (II). The H atoms were introduced for all molecules before the isotropic refinement was started. These atoms were located at a distance of 1·08 Å, sp^2 hybridization being assumed. The refinement was performed with a damping factor.

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters for all three compounds have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39850 (31 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

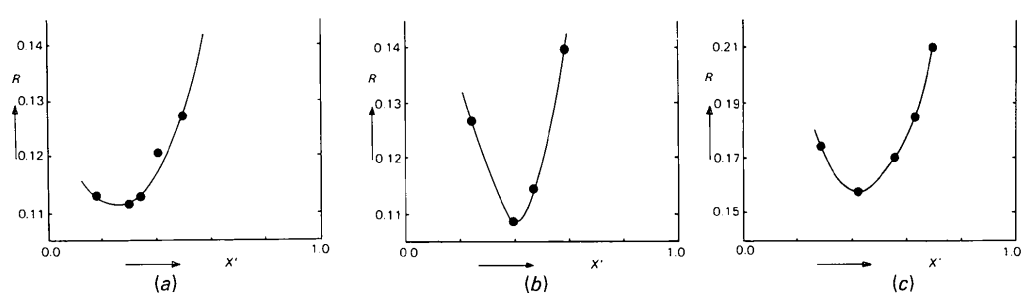

Fig. 2. The R value as a function of X'. (*a*) Mixed crystal $X = 0·26$. The lowest R value is found for $X' = 0·30$. (*b*) Mixed crystal $X = 0·56$. The lowest R value corresponds to $X' = 0·39$. (*c*) Mixed crystal $X = 0·46$. The minimum in the curve corresponds to $X' = 0·42$.

Table 1. *Positional* ($\times 10^4$) *and thermal* ($\times 10^4$) *parameters with their e.s.d.'s in parentheses*

$$U_{eq} = \tfrac{1}{3}\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

(*a*) Mixed crystal $X = 0{\cdot}26$ ($X' = 0{\cdot}30$)

Molecule *A*1 (*trans*-stilbene), occupancy factor = 0·16

	x	*y*	*z*	U_{eq}(Å^2)
C(1)	4717 (7)	883 (12)	4989 (6)	460
C(2)	4267 (5)	1313 (9)	5841 (6)	434
C(3)	3738 (5)	3328 (9)	5726 (6)	518
C(4)	3221 (5)	3724 (9)	6424 (6)	573
C(5)	3228 (5)	2108 (9)	7258 (6)	577
C(6)	3761 (5)	110 (9)	7398 (6)	543
C(7)	4276 (5)	−285 (9)	6704 (6)	477

Molecule *B*1 (*trans*-stilbene), occupancy factor 0·32

	x	*y*	*z*	U_{eq}(Å^2)
C(8)	9661 (4)	710 (9)	9674 (2)	589
C(9)	9154 (3)	595 (7)	8388 (2)	527
C(10)	9267 (3)	−1243 (7)	7712 (2)	604
C(11)	8758 (3)	−1284 (7)	6497 (2)	655
C(12)	8133 (3)	512 (7)	5960 (2)	652
C(13)	8020 (3)	2350 (7)	6637 (2)	686
C(14)	8531 (3)	2390 (7)	7852 (2)	626

Molecule *B*2 (*trans*-stilbene), occupancy factor 0·04

	x	*y*	*z*	U_{eq}(Å^2)
C(15)	9908	−676	9529	589
C(16)	9262	−132	8318	527
C(17)	9135	−1553	7347	604
C(18)	8530	−867	6224	655
C(19)	8052	1241	6072	652
C(20)	8181	2661	7044	686
C(21)	8784	1975	8165	626

Molecule *A*2 (*trans*-azobenzene), occupancy factor 0·84

	x	*y*	*z*	U_{eq}(Å^2)
N(22)	4893 (1)	1032 (2)	5041 (2)	464 (7)
C(23)	4320 (1)	1343 (2)	5723 (1)	431 (8)
C(24)	3856 (1)	3453 (2)	5583 (1)	526 (10)
C(25)	3295 (1)	3909 (2)	6220 (1)	581 (11)
C(26)	3216 (1)	2302 (2)	7014 (1)	561 (11)
C(27)	3705 (1)	−219 (2)	7174 (1)	546 (10)
C(28)	4259 (1)	−281 (2)	6525 (1)	477 (9)

Molecule *B*3 (*trans*-azobenzene), occupancy factor 0·53

	x	*y*	*z*	U_{eq}(Å^2)
N(29)	9721 (2)	809 (4)	9775 (1)	583 (14)
C(30)	9216 (2)	582 (4)	8529 (1)	531 (15)
C(31)	9290 (2)	−1294 (4)	7852 (1)	615 (17)
C(32)	8768 (2)	−1324 (4)	6640 (1)	657 (19)
C(33)	8172 (2)	521 (4)	6105 (1)	651 (19)
C(34)	8099 (2)	2398 (4)	6783 (1)	674 (19)
C(35)	8620 (2)	2428 (4)	7995 (1)	638 (18)

Molecule *B*4 (*trans*-azobenzene), occupancy factor 0·11

	x	*y*	*z*	U_{eq}(Å^2)
N(36)	9958	−734	9607	589
C(37)	9286	−108	8474	527
C(38)	9201	−1637	7557	604
C(39)	8631	−1068	6400	655
C(40)	8145	1032	6160	652
C(41)	8228	2560	7076	686
C(42)	8798	1990	8234	626

(*b*) Mixed crystal $X = 0{\cdot}56$ ($X' = 0{\cdot}39$)

Molecule *A*1 (*trans*-stilbene), occupancy factor 0·44

	x	*y*	*z*	U_{eq}(Å^2)
C(1)	4737 (2)	917 (4)	4998 (3)	490
C(2)	4242 (2)	1330 (4)	5793 (2)	453
C(3)	3724 (2)	3364 (4)	5661 (2)	534
C(4)	3194 (2)	3785 (4)	6331 (2)	596
C(5)	3179 (2)	2176 (4)	7155 (2)	600
C(6)	3700 (2)	159 (4)	7312 (2)	584
C(7)	4228 (2)	−261 (4)	6645 (2)	507

Molecule *B*1 (*trans*-stilbene), occupancy factor 0·60

	x	*y*	*z*	U_{eq}(Å^2)
C(8)	9713 (2)	802 (4)	9670 (1)	596 (13)
C(9)	9169 (1)	666 (4)	8404 (1)	523 (11)
C(10)	9248 (1)	−1176 (4)	7710 (1)	591 (13)
C(11)	8734 (1)	−1162 (4)	6506 (1)	637 (14)
C(12)	8139 (1)	692 (4)	5996 (1)	625 (13)
C(13)	8059 (1)	2534 (4)	6692 (1)	699 (15)
C(14)	8574 (1)	2521 (4)	7897 (1)	646 (13)

Molecule *B*2 (*trans*-stilbene), occupancy factor 0·08

	x	*y*	*z*	U_{eq}(Å^2)
C(15)	9909	−679	9532	589
C(16)	9274	−132	8330	515
C(17)	9149	−1559	7365	580
C(18)	8550	−870	6249	609
C(19)	8078	1245	6098	617
C(20)	8205	2672	7064	671
C(21)	8803	1983	8179	638

Molecule *A*2 (*trans*-azobenzene), occupancy factor 0·56

	x	*y*	*z*	U_{eq}(Å^2)
N(22)	4893 (2)	1029 (2)	5051 (2)	495 (9)
C(23)	4313 (1)	1318 (3)	5716 (2)	455 (10)
C(24)	3850 (1)	3428 (3)	5574 (2)	553 (13)
C(25)	3299 (1)	3885 (3)	6213 (2)	621 (14)
C(26)	3230 (1)	2277 (3)	7010 (2)	629 (15)
C(27)	3718 (1)	193 (3)	7173 (2)	598 (14)
C(28)	4262 (1)	−307 (3)	6521 (2)	515 (12)

Molecule *B*3 (*trans*-azobenzene), occupancy factor 0·26

	x	*y*	*z*	U_{eq}(Å^2)
N(29)	9678 (3)	714 (8)	9777 (1)	589
C(30)	9218 (3)	484 (6)	8536 (1)	515
C(31)	9307 (3)	−1439 (6)	7896 (1)	580
C(32)	8802 (3)	−1540 (6)	6690 (1)	617
C(33)	8209 (3)	282 (6)	6124 (1)	609
C(34)	8119 (3)	2205 (6)	6766 (1)	671
C(35)	8625 (3)	2306 (6)	7972 (1)	638

Molecule *B*4 (*trans*-azobenzene), occupancy factor 0·06

	x	*y*	*z*	U_{eq}(Å^2)
N(36)	9930	−773	9620	589
C(37)	9295	−109	8484	515
C(38)	9211	−1643	7572	580
C(39)	8648	−1072	6423	609
C(40)	8168	1037	6148	617
C(41)	8249	2570	7095	671
C(42)	8813	1998	8245	638

(*c*) Mixed crystal $X = 0{\cdot}46$ ($X' = 0{\cdot}42$)

Molecule *A*1 (*trans*-stilbene), occupancy factor 0·37

	x	*y*	*z*	U_{eq}(Å^2)
C(1)	4724 (9)	887 (14)	4999 (8)	426 (12)
C(2)	4281 (5)	1302 (9)	5854 (6)	373 (13)
C(3)	3727 (5)	3273 (9)	5722 (6)	444 (14)
C(5)	3202 (5)	3623 (9)	6408 (6)	429 (15)
C(4)	3225 (5)	2006 (8)	7246 (5)	495 (17)
C(6)	3783 (5)	56 (9)	7407 (6)	409 (13)
C(7)	4306 (5)	−296 (9)	6721 (6)	399 (13)

Molecule *B*1 (*trans*-stilbene), occupancy factor 0·46

	x	*y*	*z*	U_{eq}(Å^2)
C(8)	9689 (11)	788 (19)	9692 (3)	547 (14)
C(9)	9153 (4)	733 (8)	8417 (2)	501 (15)
C(10)	9255 (4)	−1048 (8)	7704 (2)	459 (16)
C(11)	8729 (4)	−1021 (8)	6500 (2)	477 (16)
C(12)	8102 (4)	789 (8)	6009 (2)	479 (16)
C(13)	8001 (4)	2571 (8)	6721 (2)	542 (16)
C(14)	8526 (4)	2544 (8)	7925 (2)	563 (16)

Molecule *B*2 (*trans*-stilbene), occupancy factor 0·07

	x	*y*	*z*	U_{eq}(Å^2)
C(15)	9907	−673	9529	438
C(16)	9267	−118	8328	334
C(17)	9142	−1542	7362	465
C(18)	8543	−857	6244	466
C(19)	8067	1254	6091	474
C(20)	8192	2678	7058	447
C(21)	8792	1993	8175	376

Molecule *A*2 (*trans*-azobenzene), occupancy factor 0·63

	x	*y*	*z*	U_{eq}(Å^2)
N(22)	4900 (3)	1035 (2)	5048 (5)	426 (12)
C(23)	4301 (3)	1356 (6)	5686 (4)	373 (13)
C(24)	3855 (3)	3490 (6)	5547 (4)	443 (14)
C(25)	3300 (3)	3981 (6)	6180 (4)	429 (15)
C(26)	3209 (3)	2382 (6)	6969 (4)	495 (17)
C(27)	3681 (3)	274 (6)	7128 (4)	409 (13)
C(28)	4222 (3)	−258 (6)	6482 (4)	399 (13)

Molecule *B*3 (*trans*-azobenzene), occupancy factor 0·39

	x	*y*	*z*	U_{eq}(Å^2)
N(29)	9724 (9)	803 (15)	9752 (2)	547 (14)
C(30)	9234 (5)	468 (8)	8522 (2)	501 (15)
C(31)	9308 (5)	−1517 (8)	7911 (2)	459 (16)
C(32)	8809 (5)	−1668 (8)	6704 (2)	477 (16)
C(33)	8236 (5)	162 (8)	6107 (2)	479 (16)
C(34)	8160 (5)	2146 (8)	6717 (2)	542 (16)
C(35)	8660 (5)	2299 (8)	7924 (2)	563 (16)

Molecule *B*4 (*trans*-azobenzene), occupancy factor 0·08

	x	*y*	*z*	U_{eq}(Å^2)
N(36)	9915	−772	9612	438
C(37)	9280	−110	8479	334
C(38)	9202	−1641	7566	465
C(39)	8641	−1067	6414	466
C(40)	8155	1035	6174	474
C(41)	8233	2566	7086	447
C(42)	8796	1994	8238	376

Although neutron scattering of H is more pronounced than X-ray scattering of H and in addition the positions of the H atoms of *trans*-azobenzene and *trans*-stilbene molecules are less similar than that of the non-hydrogen atoms, it appeared that the distribution of *trans*-stilbene between site *A* and site *B* could not be refined. So the isotropic refinement was again carried out with several values for X'. As is shown in Fig. 2(*c*) the lowest *R* value (0·148) was obtained with $X' = 0{\cdot}42$. The occupancy factors are given in Table 1. At this stage an absorption correction was applied: we preferred an empirical absorption correction due to the irregular shape of the crystal. The absorption correction was carried out with *DIFABS* (Walker & Stuart, 1983). Anisotropic block refinement started at an *R* value of 0·141. In contrast to the preceding refinement the H atoms were refined anisotropically. During the final stage of refinement the anisotropic thermal parameters of molecules *B*2 and *B*4 were replaced by the corresponding U_{eq}. *R* dropped to 0·082; the number of variables was 193 ($R_w = 0{\cdot}072$, $S = 0{\cdot}39$). Mean Δ/σ and max. Δ/σ are 0·15 and 0·83 respectively. In the final difference map max. peak and min. trough were 0·10 and −0·09 fm Å^{-3} respectively. The neutron scattering lengths used for C, N and H are 0·665, 0·94 and −0·374 fm.

Calculations carried out on the CDC-Cyber 175 computer of the University of Utrecht with *SHELX*76 (Sheldrick, 1976) and programs of the *APOLLO* (data reduction and corrections; A. L. Spek) and *EUCLID* (calculation of geometrical data and illustrations; Spek, 1982) packages.

Discussion. From Fig. 3 it can be seen that the lattice parameters of the mixed crystals almost obey Vegard's Law. Consequently the excess volume of these crystals is almost zero.

A survey of the bond distances and bond angles obtained, together with their constrained values, is given in Table 2.

In Table 3 the relevant torsion angles, that were not constrained, are shown; the molecules at both independent sites prefer an almost planar conformation. From

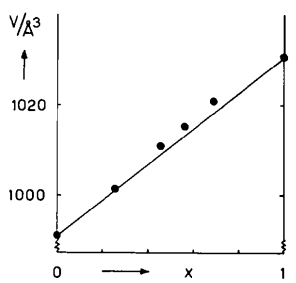

Fig. 3. Graph of the unit-cell volume as a function of the mole fraction (*X*) of *trans*-stilbene.

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

Molecules *B*2 and *B*4 are not included. Superscripts indicate symmetry-related units according to the following code: (i) $1-x$, $-y$, $1-z$; (ii) $2-x$, $-y$, $2-z$.

	$X = 0{\cdot}26$	$X = 0{\cdot}56$	$X = 0{\cdot}46$	Restraint
Molecule *A*1*				
C(1)–C(1^{i})	1·331 (12)	1·331 (4)	1·329 (14)	1·33
C(1)–C(2)	1·470 (12)	1·470 (5)	1·471 (14)	1·471
C(2)–C(1)–C(1^{i})	126·1 (7)	126·6 (3)	126·3 (9)	126·1
C(1)–C(2)–C(3)	118·6 (6)	118·6 (2)	118·5 (7)	118·6
C(1)–C(2)–C(7)	123·3 (6)	122·5 (5)	123·3 (6)	123·2
Mean intraring bond length	1·389 (7)	1·389 (7)	1·389 (7)	
Mean intraring bond angle	120 (1)	120 (1)	120 (1)	
Molecule *A*2*				
N(22)–N(22^{i})	1·249 (2)	1·248 (2)	1·248 (3)	1·250
N(22)–C(23)	1·431 (3)	1·433 (4)	1·429 (8)	1·429
N(22^{i})–N(22)–C(23)	113·7 (2)	114·5 (2)	114·1 (4)	113·8
N(22)–C(23)–C(24)	115·8 (1)	115·8 (2)	116·1 (4)	116·2
N(22)–C(23)–C(28)	123·2 (1)	123·1 (2)	123·0 (3)	122·9
Mean intraring bond length	1·387 (4)	1·386 (4)	1·386 (3)	
Mean intraring bond angle	120·0 (7)	120·0 (7)	120·0 (7)	
Molecule *B*1†				
C(8^{ii})–C(8)	1·330 (8)	1·326 (4)	1·331 (19)	1·330
C(8)–C(9)	1·471 (5)	1·469 (3)	1·473 (11)	1·471
C(8^{ii})–C(8)–C(9)	126·4 (4)	126·8 (2)	126·0 (8)	126·1
C(8)–C(9)–C(10)	122·5 (4)	122·9 (2)	122·2 (6)	122·4
C(8)–C(9)–C(14)	117·6 (4)	117·0 (2)	117·8 (6)	117·5
Molecule *B*3†				
N(29^{ii})–N(29)	1·246 (4)	1·249 (6)	1·250 (15)	1·25
N(29)–C(30)	1·432 (3)	1·429 (4)	1·427 (10)	1·429
N(29^{ii})–N(29)–C(30)	114·1 (2)	113·9 (3)	114·2 (7)	113·8
N(29)–C(30)–C(31)	124·8 (2)	124·2 (3)	124·3 (6)	121·3
N(29)–C(30)–C(35)	115·2 (2)	115·7 (3)	115·8 (5)	116·2

* Intraring bond angles and intraring bond lengths are put equal to those of the pure components and fixed during the refinement; numbers in parentheses refer to standard deviations in the mean of the values used.

† Intraring bond angles 120°; intraring bond lengths 1·395 Å.

Table 3. *Selected torsion angles* (°) *of molecules A*1, *A*2, *B*1 *and B*3 *with their e.s.d.'s in parentheses*

Mixed crystals		
$X = 0{\cdot}26$		
C(1^{i})–C(1)–C(2)–C(3)	176·2 (8)	175·0 (2)
C(1^{i})–C(1)–C(2)–C(7)	−9·3 (13)	−5·3 (2)
C(8^{ii})–C(8)–C(9)–C(10)	7·5 (8)	3·6 (2)
C(8^{ii})–C(8)–C(9)–C(14)	−173·7 (5)	−176·1 (2)
N(22^{i})–N(22)–C(23)–C(24)	−163·2 (2)	−164·1 (1)
N(22^{i})–N(22)–C(23)–C(28)	20·1 (2)	17·5 (2)
N(29^{ii})–N(29)–C(30)–C(31)	2·6 (4)	7·1 (2)
N(29^{ii})–N(29)–C(30)–C(35)	−177·1 (2)	−173·2 (1)
$X = 0{\cdot}56$		
C(1^{i})–C(1)–C(2)–C(3)	179·8 (3)	
C(1^{i})–C(1)–C(2)–C(7)	−3·2 (5)	
C(8^{ii})–C(8)–C(9)–C(10)	−4·8 (4)	
C(8^{ii})–C(8)–C(9)–C(14)	177·1 (2)	
N(22^{i})–N(22)–C(23)–C(24)	−162·4 (2)	
N(22^{i})–N(22)–N(23)–C(28)	22·4 (4)	
N(29^{ii})–N(29)–C(30)–C(31)	14·4 (6)	
N(29^{ii})–N(29)–C(30)–C(35)	−167·9 (4)	
$X = 0{\cdot}46$		
C(1^{i})–C(1)–C(2)–C(3)	179·5 (10)	
C(1^{i})–C(1)–C(2)–C(7)	−7·4 (16)	
C(8^{ii})–C(8)–C(9)–C(10)	−0·3 (17)	
C(8^{ii})–C(8)–C(9)–C(14)	179·7 (11)	
N(22^{i})–N(22)–C(23)–C(24)	−162·9 (5)	
N(22^{i})–N(22)–C(23)–C(28)	22·7 (7)	
N(29^{ii})–N(29)–C(30)–C(31)	3·5 (13)	
N(29^{ii})–N(29)–C(30)–C(35)	−175·7 (9)	

Table 1 it can be inferred that the thermal motion at site B is larger than that at site A probably due to more available space at site B. This difference in thermal motion is also observed in the crystals of the pure substances. The relatively high R value found for the crystal with $X = 0{\cdot}46$ is probably due to the large number of H atoms: during neutron diffraction these atoms cause incoherent neutron background scattering. Moreover, the mixed crystal used was of minimal size which caused a data set with predominantly weak intensities.

In Fig. 4(*a*) *trans*-azobenzene and *trans*-stilbene at site A are drawn. From this figure it is clear that these molecules almost overlap. In Figs. 4(*b*) and 4(*c*) *ORTEP* drawings (Johnson, 1971) of the disordered molecules of *trans*-azobenzene and *trans*-stilbene at site B, along with their numbering scheme, are shown. It can be concluded that the molecules at site B show the same kind of disorder as that of the pure components. From Fig. 4(*b*) it is clear that the H atoms attached to the ethene bond of stilbene are the only atoms which do not overlap with azobenzene atoms. To determine more accurately the distribution of stilbene a difference Fourier map was calculated in which these H atoms were not included in the structure factor calculations. The intensity data for the mixed crystal with $X = 0{\cdot}46$ were used because the neutron scattering of H is larger than the X-ray scattering of H. Since the positions of H(8) and H(15^{ii}) are very similar (see Fig. 4*c*) this difference map exhibits two maxima: one at the position of H(1) and a second higher maximum at the positions of H(8) and H(15^{ii}) (see Fig. 5). Integration of these two peaks results in a density ratio of 64:36, which indicates that 36% of the total amount of stilbene is added at site A. This agrees very well with the distributions of stilbene molecules corresponding to the lowest R values obtained by the isotropic refinement (see Table 1). So it might be concluded that *trans*-stilbene is preferentially substituted at site B. As is mentioned before, site B has more available space than site A (256 *vs* 252 $Å^3$ respectively). With van der Waals radii the volumes of *trans*-azobenzene and *trans*-stilbene are 172 and 180 $Å^3$ respectively. Comparison of these values, which are calculated with *SPACE* (Schreurs & Spek, 1985), leads to the conclusion that the larger stilbene molecule is preferentially substituted at site B which takes up the greater volume. It is intended to supplement these findings, which in spite of some experimental and refinement problems are fairly conclusive, with atom–atom potential calculations.

The investigations were supported in part by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization for the Advancement of Pure Research (ZWO). We thank Drs A. J. M. Duisenberg for collecting the X-ray intensity data.

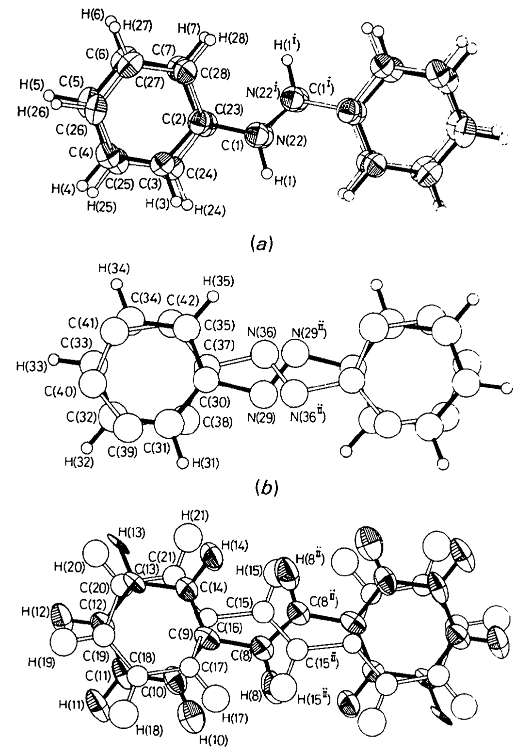

Fig. 4. (*a*) A composite view of molecules $A1$ (*trans*-stilbene) and $A2$ (*trans*-azobenzene) in the mixed crystal $X = 0{\cdot}56$. 50% probability plots of thermal ellipsoids of molecules $A1$ and $A2$. (*b*) View of disordered molecules $B3$ and $B4$ in the mixed crystal $X = 0{\cdot}56$. (*c*) A composite view of the disordered stilbene molecules at site B of the mixed crystal $X = 0{\cdot}46$. 50% probability plots for thermal ellipsoids of molecule $B1$.

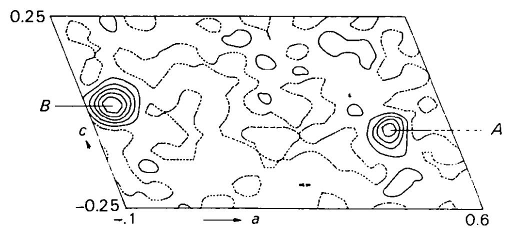

Fig. 5. A difference electron density map of the mixed crystal ($X = 0{\cdot}46$) drawn with *SPACE* (Schreurs & Spek, 1985). The H atoms belonging to the ethene moiety of *trans*-stilbene are not included in F_c. A: peak located at the position of H(1). B: peak located at the positions of H(8) and H(15^{ii}).

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cis-6,11,17,18-Tetrahydro-5,12-dioxatribenzo[*a,e,i*]cyclododecene-17,18-diol, $C_{22}H_{20}O_4$

BY FRANK R. FRONCZEK, STEVEN J. JUNGK AND RICHARD D. GANDOUR*

Department of Chemistry, Louisiana State University, Baton Rouge, LA 70803-1804, *USA*

(*Received* 10 *July* 1984; *accepted* 30 *October* 1984)

Abstract. $M_r = 348{\cdot}4$, triclinic, $P\bar{1}$, $a = 8{\cdot}633$ (1), $b = 9{\cdot}035$ (1), $c = 11{\cdot}957$ (1) Å, $\alpha = 74{\cdot}11$ (1), $\beta = 73{\cdot}61$ (1), $\gamma = 83{\cdot}00$ (1)°, $V = 859{\cdot}5$ (2) Å^3, $Z = 2$, $D_x = 1{\cdot}346$ g cm^{-3}, $\lambda = 0{\cdot}71073$ Å, μ(Mo $K\alpha$) = $0{\cdot}86$ cm^{-1}, $F(000) = 368{\cdot}0$, $T = 296$ K, $R = 0{\cdot}031$ for 2016 observations (of 3010 unique data). The diol O atoms form a *gauche* interaction with O—C—C—O torsion angle, 42·5 (3)°, smaller than that in related compounds. Both intramolecular and intermolecular hydrogen bonding are present.

Introduction. During the course of our studies preparing stilbene cycles as backbones for intramolecular reactions (Tirado-Rives, Oliver, Fronczek & Gandour, 1984), the title compound has been isolated and its crystal structure has been determined.

Experimental. Title compound isolated from mixture produced in the reaction of 2,2′-[*o*-phenylenebis(methyleneoxy)]dibenzaldehyde with $TiCl_4$/BuLi. Colorless plates from evaporation of $CHCl_3$, m.p. 455–458 K. D_m not determined. Crystal size $0{\cdot}20 \times 0{\cdot}42 \times 0{\cdot}60$ mm. Space-group determination by successful refinement of centrosymmetric model. Cell dimensions from setting angles of 25 reflections having $13° > \theta > 12°$. Data collection on Enraf–Nonius CAD-4 diffractometer, Mo $K\alpha$ radiation, graphite monochromator, ω–2θ scans designed for $I = 50\sigma(I)$. Scan rates varied 0·57–20·0° min^{-1}. Reflections having $1° < \theta < 25°$, $0 \le h \le 10$, $-10 \le k \le 10$, $-13 \le l \le 13$ (excluding redundant data) measured, corrected for background, Lorentz, and polarization effects. Maximum value of $(\sin\theta)/\lambda = 0{\cdot}59$ Å^{-1}. Three standard reflections, ±1·6% random variation. Absorption negligible. Structure solved using *MULTAN*78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978), refined by full-matrix least squares based upon F, using data for which $I > 3\sigma(I)$ (994 unobserved reflections), weights $w = \sigma^{-2}(F_o)$, with the Enraf–Nonius *SDP* (Frenz & Okaya, 1980). Non-H atoms anisotropic; H atoms located by ΔF synthesis and refined isotropically. Final $R = 0{\cdot}031$, $R_w = 0{\cdot}043$, $S = 1{\cdot}413$ for 316 variables. Maximum shift $0{\cdot}02\sigma$ in final cycle, largest residual density 0·16 e Å^{-3}, extinction coefficient $3{\cdot}0\ (3) \times 10^{-6}$.

Discussion. The atomic parameters are given in Table 1.† Selected torsion angles are given in Fig. 1.

There are some noteworthy values for the angles and torsion angles associated with the diol C atoms. The angles, C(9)—C(8)—C(7) and C(6)—C(7)—C(8), are 115·4 (1) and 115·6 (1)°, respectively, which are significant distortions from their expected tetrahedral values. The torsion angles about C(7)—C(8) are surprising in that the *gauche* interactions are nearly 20° less than the typical values. This conformation brings the two hydroxyl O atoms within 2·689 (1) Å of each other. While no torsional motion about C(7)—C(8) can produce a linear intramolecular hydrogen bond, the observed twist brings the H atom on O(3) to a position equidistant from the plane defined by C(7), O(3), and O(4), and the plane bisecting the C(8)—O(4)—H(40) angle: 0·35 (2) Å from each. The O(3)—H(30)···O(4)

* To whom correspondence should be addressed.

† Tables of distances and angles, H-atom coordinates. H-atom distances and angles, anisotropic thermal parameters, deviations from least-squares planes, and structure factor amplitudes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39872 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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