Molecular Motion and Conformational Interconversion of Azobenzenes in Crystals as Studied by X-ray Diffraction

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Abstract

Crystal structures of (E)-azobenzene (1), (E)-2,2'-dimethylazobenzene (2), (E)-3,3'-dimethylazobenzene (3) and (E)-4,4'-dimethylazobenzene (4) were determined by X-ray diffraction at various temperatures. An apparent shrinkage of the N=N bond and its temperature dependence were observed and are interpreted in terms of an artifact caused by the torsional vibration of the N—Ph bonds in crystals. In the crystal structures of (1), (3) and (4) the dynamic disorder was observed. The disorder is accounted for by the torsional vibration whose amplitude is large enough to give rise to the conformational interconversion. No disorder was observed for a crystal of (2). This is ascribed to the large difference in energy of the two conformers as free molecules. The true length of the N=N bond in azobenzenes was estimated to be 1.26–1.27 Å.

1. Introduction

Dynamic behaviour of (E)-azobenzenes in the solid state has been a subject of substantial interest and studied by various methods: photokinematical approach (Ghoshal, Sarkar & Kastha, 1983); calorimetry (Saito, Yamamura, Kikuchi & Ikemoto, 1995); NMR (Ueda, Nakamura & Chihara, 1988); NQR (Eguchi, Kishita, Nakamura & Chihara, 1988; Eguchi, Mano & Nakamura, 1989). However, a concrete picture of the molecular motion has not yet been obtained due to the lack of information on the crystal structures at different temperatures.

The crystal structure of (E)-azobenzene (1) has been determined only at room temperature by several groups (de Lange, Robertson & Woodward, 1939; Brown, 1966a; Bouwstra, Schouten & Kroon, 1983) and it has been found that there is an orientational disorder at one of two crystallographically independent sites in the monoclinic unit cell. In the disordered site two molecules are approximately related to one another by 180° rotation around their longest axes. A similar disorder was also found in crystals of (E)-4,4'-dimethylazobenzene at room temperature (Padmanabhan, Shankar & Khubchandani, 1958;

Brown, 1966b). It has remained unclear whether the disorder is dynamic or static. If the disorder is dynamic it would be related to some molecular motions.

For the crystal structures of the closely related compounds (E)-stilbenes and 1,2-diphenylethanes it was recently shown that the central bonds of these molecules, *i.e.* ethylene and ethane bonds, are observed to be anomalously shorter than those expected from chemical intuition and that the shrinkage is an artifact caused by the torsional vibration of the C—Ph bonds in crystals (Ogawa, Sano, Yoshimura, Takeuchi & Toriumi, 1992; Ogawa, Harada & Tomoda, 1995; Harada, Ogawa & Tomoda, 1995). It is, therefore, expected that a similar phenomenon would also occur in crystals of (E)-azobenzenes.

To examine the above expectation and to characterize the disorder we carried out variable-temperature X-ray crystallographic analyses of (1) and its methylated derivatives, *i.e.* (E)-2,2'-dimethylazobenzene (2), (E)-3,3'-dimethylazobenzene (3) and (E)-4,4'-dimethylazobenzene (4). This paper will reveal that the torsional vibration of the N—Ph bonds causes not only an apparent shrinkage of the N=N bonds, but also conformational interconversion in crystals.
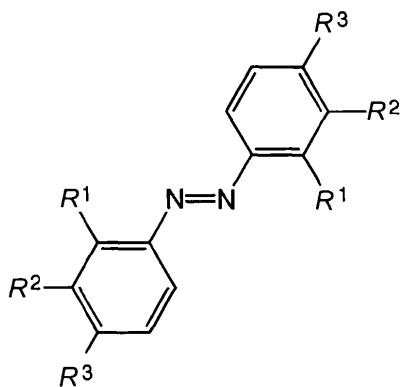
2. Experimental

Compounds (1) and (3) were purchased from Tokyo Kasei Co. Compounds (2) and (4) were synthesized according to the procedure published in the literature with a slight modification (Bigelow & Robinson, 1955). Melting points were determined on a hot stage apparatus and were uncorrected.

All diffraction measurements were made on a Rigaku AFC-6A diffractometer with graphite-monochromated Cu Kα (λ = 1.54184 Å) or Mo Kα (λ = 0.71073 Å). The low-temperature measurements were carried out using a Cryostream (Oxford Cryosystems) open-flow gas cryostat (Cosier & Glazer, 1986). The temperature was held constant within ±0.2 K during the measurement. The integrated intensities were collected in the 2θ–ω scan mode with an ω rate of 8.0° min⁻¹. The intensities were corrected for Lorentz and polarization effects, but not for absorption. Three standard reflec-

tions were measured after every 150 reflections during the data collection to monitor the decay of the crystal. No significant decrease in the intensity of the standard reflections was observed. The structures were solved by direct methods with *SHELXS*86 (Sheldrick, 1985) or *Xtal*3.4 (Hall, King & Stewart, 1995) or *SIR*92 (Altomare *et al.*, 1994). Structures were refined by full-matrix least squares on F^2 using *SHELXL*93 (Sheldrick, 1993). The weighting scheme was $w = 1/[\sigma^2(F_o^2)+(aP)^2+6P]$, where $P = (F_o^2+2F_o^2)/3$ for all the crystals. The values of a and b for each crystal are given in Table 1. For nondisordered molecules all H atoms were located from difference maps and refined isotropically, and all C atoms were refined anisotropically. For disordered molecules, the procedures of the refinement are described briefly in the next session and the details were deposited.† The crystal and experimental data are summarized in Table 1.

Quantum mechanical calculations were carried out using the density functional method (DFT) at Becke3LYP/6-32G* levels (Becke, 1993) on *Gaussian*94 (Frisch *et al.*, 1995).

is shown in Fig. 2 and the perspective views of the molecules for all compounds are shown in Fig. 3.

3.1. Crystal structure of (E)-azobenzene (1)

3.1.1. *Structure at room temperature.* The crystal structure observed at room temperature in this study is identical with that reported in the literature [monoclinic unit cell, $P2_1/a$, with $Z = 4$ (de Lange, Robertson & Woodward, 1939; Brown, 1966a; Bouwstra, Schouten & Kroon, 1983)]. There are two crystallographically independent molecules (referred to as molecules 1 and
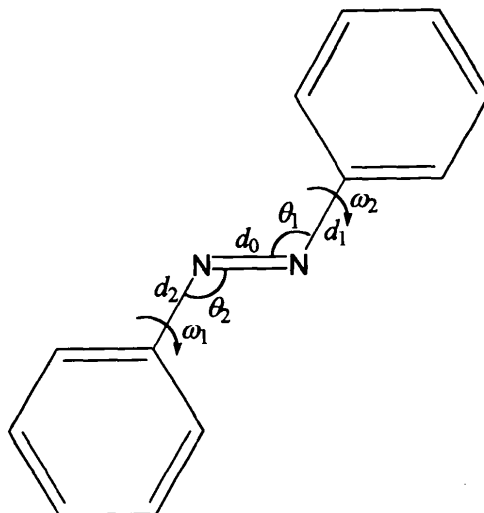
Fig. 1. Definition of the geometrical parameters for the (E)-azobenzene skeleton.

	R^1	R^2	R^3
(1)	H	H	H
(2)	Me	H	H
(3)	H	Me	H
(4)	H	H	Me

3. Results and discussion

The atomic coordinates are listed in Table 2 and the selected geometrical parameters in Table 3. The definition of the geometrical parameters is given in Fig. 1. The packing diagram for the crystal of (1)

† Lists of atomic coordinates, anisotropic displacement factors, complete geometry, structure factors and the details of the refinement with the disordered models have been deposited with the IUCr (Reference: OA0007). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Fig. 2. Projection of the crystal structure along the *b* axis, showing the disorder at site 2.

Table 1. *Experimental details*

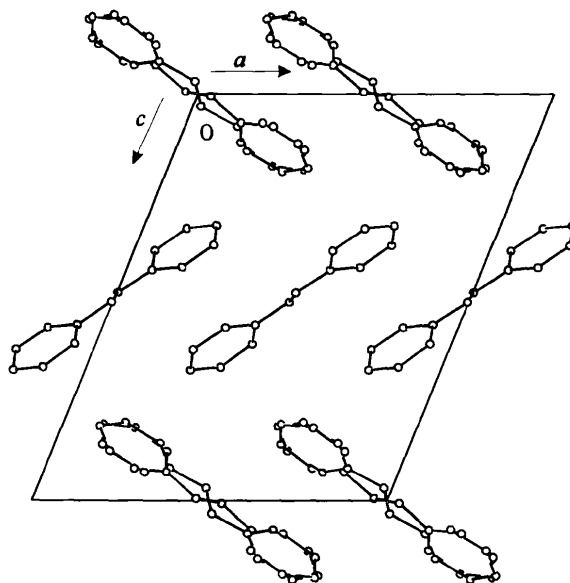|	(1) at 296 K (non-disordered medium)	(1) at 82 K	(2) at 296 K	(2) at 90 K
Crystal data				
Chemical formula	$C_{12}H_{10}N_2$	$C_{12}H_{10}N_2$	$C_{14}H_{14}N_2$	$C_{14}H_{14}N_2$
Chemical formula weight	182.22	182.22	210.28	210.28
Cell setting	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/a$	$P2_1/a$	$C2/c$	$C2/c$
a (Å)	12.1840 (11)	12.034 (2)	13.6250 (13)	13.4663 (13)
b (Å)	5.7888 (14)	5.695 (2)	6.3728 (12)	6.2940 (14)
c (Å)	15.2282 (12)	14.979 (2)	13.8825 (13)	13.6133 (12)
β (°)	112.440 (7)	112.436 (11)	97.110 (8)	98.116 (7)
V (Å³)	992.7 (3)	948.8 (4)	1196.1 (3)	1142.3 (3)
Z	4	4	4	4
D_x (Mg m^{-3})	1.219	1.276	1.168	1.223
Radiation type	Cu $K\alpha$	Mo $K\alpha$	Cu $K\alpha$	Cu $K\alpha$
Wavelength (Å)	1.54184	0.71073	1.54184	1.54184
No. of reflections for cell parameters	25	25	25	25
θ range (°)	34.5–39.7	14.5–14.9	37.6–39.5	38.5–39.9
μ (mm^{-1})	0.577	0.077	0.540	0.565
Temperature (K)	296	82	296	90
Crystal form	Block	Block	Rectangular	Rectangular
Crystal size (mm)	$0.40 \times 0.40 \times 0.40$	$0.40 \times 0.40 \times 0.40$	$0.25 \times 0.25 \times 0.20$	$0.25 \times 0.25 \times 0.20$
Crystal color	Red	Red	Orange	Orange
Data collection				
Diffractometer	Rigaku AFC-6A	Rigaku AFC-6A	Rigaku AFC-6A	Rigaku AFC-6A
Data collection method	$\theta/2\theta$ scans	$\theta/2\theta$ scans	$\theta/2\theta$ scans	$\theta/2\theta$ scans
Absorption correction	None	None	None	None
No. of measured reflections	1463	4338	933	883
No. of independent reflections	1377	4171	892	842
No. of observed reflections	1124	2912	740	745
Criterion for observed reflections	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$
R_{int}	0.0208	0.0293	0.0179	0.0190
θ_{max} (°)	59.94	35.00	59.95	59.98
Range of h, k, l	$0 \rightarrow h \rightarrow 12$	$0 \rightarrow h \rightarrow 19$	$0 \rightarrow h \rightarrow 15$	$0 \rightarrow h \rightarrow 14$
	$0 \rightarrow k \rightarrow 6$	$0 \rightarrow k \rightarrow 9$	$0 \rightarrow k \rightarrow 7$	$0 \rightarrow k \rightarrow 7$
	$-17 \rightarrow l \rightarrow 15$	$-24 \rightarrow l \rightarrow 22$	$-15 \rightarrow l \rightarrow 15$	$-15 \rightarrow l \rightarrow 15$
No. of standard reflections	3	3	3	3
Frequency of standard reflections	Every 150 reflections	Every 150 reflections	Every 150 reflections	Every 150 reflections
Intensity decay (%)	5	3	5	None
Refinement				
Refinement on	F^2	F^2	F^2	F^2
$R[F^2 > 2\sigma(F^2)]$	0.0974	0.0545	0.0620	0.0386
$wR(F^2)$	0.2007	0.1370	0.1386	0.1050
S	1.230	1.086	1.183	1.042
No. of reflections used in refinement	1377	4168	892	840
No. of parameters used	167	167	101	101
H-atom treatment	All H-atom parameters refined	All H-atom parameters refined	All H-atom parameters refined	All H-atom parameters refined
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.1423P)^2 + 0.1855P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0808P)^2 + 0.2859P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.1043P)^2 + 0.0417P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0856P)^2 + 0.3029P]$, where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$	<0.001	−0.001	−0.030	−0.005
$\Delta\rho_{max}$ (e Å^{-3})	0.428	0.511	0.268	0.184
$\Delta\rho_{min}$ (e Å^{-3})	−0.722	−0.421	−0.421	−0.292
Extinction method	None	None	None	None
Source of atomic scattering factors	*International Tables for Crystallography* (1992, Vol. C)	*International Tables for Crystallography* (1992, Vol. C)	*International Tables for Crystallography* (1992, Vol. C)	*International Tables for Crystallography* (1992, Vol. C)
Computer programs				
Data collection	*MSC/AFC* (MSC, 1988)	*MSC/AFC* (MSC, 1988)	*MSC/AFC* (MSC, 1988)	*MSC/AFC* (MSC, 1988)
Cell refinement	*MSC/AFC* (MSC, 1988)	*MSC/AFC* (MSC, 1988)	*MSC/AFC* (MSC, 1988)	*MSC/AFC* (MSC, 1988)
Data reduction	DIFDAT_ADDREF_SORTRF (*Xtal*3.4: Hall, King & Stewart, 1995)	DIFDAT_ADDREF_SORTRF (*Xtal*3.4: Hall, King & Stewart, 1995)	DIFDAT_ADDREF_SORTRF (*Xtal*3.4: Hall, King & Stewart, 1995)	DIFDAT_ADDREF_SORTRF (*Xtal*3.4: Hall, King & Stewart, 1995)
Structure solution	*SHELXS*86 (Sheldrick, 1990)	*SHELXS*86 (Sheldrick, 1990)	*SHELXS*86 (Sheldrick, 1990)	*SHELXS*86 (Sheldrick, 1990)
Structure refinement	*SHELXL*93 (Sheldrick, 1993)	*SHELXL*93 (Sheldrick, 1993)	*SHELXL*93 (Sheldrick, 1993)	*SHELXL*93 (Sheldrick, 1993)
Preparation of material for publication	*SHELXL*93 (Sheldrick, 1993)	*SHELXL*93 (Sheldrick, 1993)	*SHELXL*93 (Sheldrick, 1993)	*SHELXL*93 (Sheldrick, 1993)

Table 1. *(cont.)*

	(3) at 296 K (non-disordered medium)	(3) at 200 K	(3) at 90 K	(4) at 296 K	(4) at 90 K
Crystal data					
Chemical formula	$C_{14}H_{14}N_2$	$C_{14}H_{14}N_2$	$C_{14}H_{14}N_2$	$C_{14}H_{14}N_2$	$C_{14}H_{14}N_2$
Chemical formula weight	210.28	210.28	210.28	210.28	210.28
Cell setting	Orthorhombic	Orthorhombic	Orthorhombic	Monoclinic	Monoclinic
Space group	*Pbca*	*Pbca*	$P2_12_12_1$	$P2_1/a$	$P2_1/a$
a (Å)	13.819 (3)	13.824 (3)	11.652 (2)	11.9762 (12)	11.819 (2)
b (Å)	11.805 (3)	11.731 (2)	13.820 (2)	4.8462 (5)	4.781 (2)
c (Å)	7.5010 (12)	7.366 (2)	7.241 (2)	9.7193 (10)	9.602 (2)
β (°)				89.654 (9)	89.87 (2)
V (Å^3)	1223.6 (4)	1194.5 (4)	1166.1 (4)	564.09 (10)	542.6 (2)
Z	4	4	4	2	2
D_x (Mg m^{-3})	1.141	1.169	1.198	1.238	1.287
Radiation type	Mo $K\alpha$	Cu $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
Wavelength (Å)	0.71073	1.54184	0.71073	0.71073	0.71073
No. of reflections for cell parameters	25	25	25	25	25
θ range (°)	10.4–11.3	38.0–39.9	12.4–14.9	13.9–14.8	10.2–14.8
μ (mm^{-1})	0.068	0.540	0.072	0.074	0.077
Temperature (K)	296	200	90	296	90
Crystal form	Rectangular	Rectangular	Rectangular	Block	Block
Crystal size (mm)	0.30 × 0.30 × 0.25	0.30 × 0.30 × 0.25	0.30 × 0.30 × 0.25	0.40 × 0.40 × 0.35	0.40 × 0.40 × 0.35
Crystal color	Red	Red	Red	Orange	Orange
Data collection					
Diffractometer	Rigaku AFC-6A	Rigaku AFC-6A	Rigaku AFC-6A	Rigaku AFC-6A	Rigaku AFC-6A
Data collection method	$\theta/2\theta$ scans	$\theta/2\theta$ scans	$\theta/2\theta$ scans	$\theta/2\theta$ scans	$\theta/2\theta$ scans
Absorption correction	None	None	None	None	None
No. of measured reflections	1403	738	2912	1733	3680
No. of independent reflections	1403	738	2912	1646	2395
No. of observed reflections	637	634	1874	1042	1825
Criterion for observed reflections	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$
R_{int}	–	–	–	0.0302	0.0251
θ_{max} (°)	27.49	59.82	35.00	30.00	34.97
Range of h, k, l	$0 \rightarrow h \rightarrow 17$	$0 \rightarrow h \rightarrow 14$	$0 \rightarrow h \rightarrow 18$	$-16 \rightarrow h \rightarrow 16$	$-19 \rightarrow h \rightarrow 19$
	$0 \rightarrow k \rightarrow 15$	$0 \rightarrow k \rightarrow 13$	$0 \rightarrow k \rightarrow 22$	$0 \rightarrow k \rightarrow 6$	$-7 \rightarrow k \rightarrow 7$
	$-9 \rightarrow l \rightarrow 0$	$-8 \rightarrow l \rightarrow 0$	$0 \rightarrow l \rightarrow 11$	$-13 \rightarrow l \rightarrow 0$	$0 \rightarrow l \rightarrow 15$
No. of standard reflections	3	3	3	3	3
Frequency of standard reflections	Every 150 reflections	Every 150 reflections	Every 150 reflections	Every 150 reflections	Every 150 reflections
Intensity decay (%)	5	None	None	3	None
Refinement					
Refinement on	F^2	F^2	F^2	F^2	F^2
$R[F^2 > 2\sigma(F^2)]$	0.0516	0.0645	0.0464	0.0665	0.0570
$wR(F^2)$	0.1252	0.1509	0.1148	0.1678	0.1494
S	1.200	1.280	1.083	1.140	1.169
No. of reflections used in refinement	1403	738	2911	1646	2395
No. of parameters used	101	101	201	117	112
H-atom treatment	All H-atom parameters refined	All H-atom parameters refined	All H-atom parameters refined	H atoms were ridden on the bonded C atoms.	H atoms were ridden on the bonded C atoms.
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0711P)^2 + 0.0623P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0930P)^2 + 0.2183P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0792P)^2 + 0.0000P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.1136P)^2 + 0.0257P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0873P)^2 + 0.1219P]$, where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$	−0.131	−0.073	−0.004	0.269	−0.020
$\Delta\rho_{max}$ (e Å^{-3})	0.139	0.376	0.386	0.322	0.343
$\Delta\rho_{min}$ (e Å^{-3})	−0.190	−0.566	−0.297	−0.406	−0.501
Extinction method	None	None	None	None	None
Source of atomic scattering factors	*International Tables for Crystallography* (1992, Vol. C)	*International Tables for Crystallography* (1992, Vol. C)	*International Tables for Crystallography* (1992, Vol. C)	*International Tables for Crystallography* (1992, Vol. C)	*International Tables for Crystallography* (1992, Vol. C)

2 hereafter) at sites 1 and 2 (Fig. 2). Both molecules have C_i symmetry. The geometry of molecule 1 seems to be normal. Molecule 2 is orientationally disordered (Fig. 4).

The orientational disorder could not be resolved if the usual refinement and difference-Fourier synthesis are used. This is probably due to the low resolution of the data and low population of the misorientated molecule.

Table 1 (cont.)

	(3) at 296 K (non-disordered medium)	(3) at 200 K	(3) at 90 K	(4) at 296 K	(4) at 90 K
Computer programs					
Data collection	MSC/AFC (MSC, 1988)	MSC/AFC (MSC, 1988)	MSC/AFC (MSC, 1988)	MSC/AFC (MSC, 1988)	MSC/AFC (MSC, 1988)
Cell refinement	MSC/AFC (MSC, 1988)	MSC/AFC (MSC, 1988)	MSC/AFC (MSC, 1988)	MSC/AFC (MSC, 1988)	MSC/AFC (MSC, 1988)
Data reduction	DIFDAT_ADDREF_SORTRF (Xtal3.4: Hall, King & Stewart, 1995)	DIFDAT_ADDREF_SORTRF (Xtal3.4: Hall, King & Stewart, 1995)	DIFDAT_ADDREF_SORTRF (Xtal3.4: Hall, King & Stewart, 1995)	DIFDAT_ADDREF_SORTRF (Xtal3.4: Hall, King & Stewart, 1995)	DIFDAT_ADDREF_SORTRF (Xtal3.4: Hall, King & Stewart, 1995)
Structure solution	SIR92 (Altomare et al., 1994)	SIR92 (Altomare et al., 1994)	GENTAN (Xtal3.4: Hall, King & Stewart, 1995)	SHELXS86 (Sheldrick, 1990)	SHELXS86 (Sheldrick, 1990)
Structure refinement	SHELXL93 (Sheldrick, 1993)	SHELXL93 (Sheldrick, 1993)	SHELXL93 (Sheldrick, 1993)	SHELXL93 (Sheldrick, 1993)	SHELXL93 (Sheldrick, 1993)
Preparation of material for publication	SHELXL93 (Sheldrick, 1993)	SHELXL93 (Sheldrick, 1993)	SHELXL93 (Sheldrick, 1993)	SHELXL93 (Sheldrick, 1993)	SHELXL93 (Sheldrick, 1993)

The nonresolved structure has the following geometrical features, which serve as a key to the detection of the disorder. The atomic position of N(A) is displaced from the true position toward the position of N(B) (Fig. 4). Thereby, the observed length of the N=N bond becomes shorter and that of the N—Ph bonds longer than the true lengths. The displacement of the positions of the other atoms is so small that the observed lengths between these atoms are only marginally affected. It is well known that thermal motion of molecules in crystals often results in an apparent shrinkage of bond lengths, but no elongation (Cruickshank, 1956; Dunitz, 1979; Dunitz, Schomaker & Trueblood, 1988; Dunitz, Maverick & Trueblood, 1988). The elongation of the N—Ph bonds is, therefore, decisive proof of the presence of the disorder.

Comparison of the bond lengths in molecules 1 and 2 clearly indicates the presence of the disorder at site 2 (Table 3). Thus, each length of the N=N bond [1.189(6) Å] and the N—Ph bond [1.473(4) Å] in molecule 2 is considerably shorter and longer, respectively, than the corresponding one in molecule 1 [1.249(4) and 1.431(4) Å, respectively]. A disordered model was then applied to molecule 2. Atomic coordinates reported by Bouwstra (Bouwstra, Schouten & Kroon, 1983) were used as the initial geometry. The benzene rings of the two molecules at site 2 were refined as regular hexagons. The structure of the central part [C(Ph)—N=N—C(Ph)] of the molecule was refined with restraints. The degree of misorientation was determined to be 18.5(9)%, which agrees with the reported value of 17(1)% (Bouwstra, Schouten & Kroon, 1983).

3.1.2. *Structure at low temperature.* The structure of (1) at 82 K was determined using the same crystalline specimen that was used for the room-temperature measurement. A phase transition of the solid state of (1) at 85-90 K has been suggested from a 'photokinematical approach' (Ghoshal, Sarkar & Kastha, 1983), NMR (Ueda, Nakamura & Chihara, 1988) and NQR (Eguchi, Kishita, Nakamura & Chihara, 1988; Eguchi,

Mano & Nakamura, 1989). In our diffraction measurement, however, any phase transition could not be observed between room temperature and 82 K. This result is consistent with that of the calorimetric measurement (Saito, Yamamura, Kikuchi & Ikemoto, 1995), by which the phase transition could not be detected in the temperature range 8-303 K.

In contrast to the structure at room temperature there was no indication of the disorder. Thus, the observed length of the N—Ph bonds in molecule 2 [1.431(2) Å] is much shorter than that at room temperature and equal to that in molecule 1 [1.431(1) Å]. The disorder, which disappeared at 82 K, is therefore proved to be dynamic. Accordingly, the site occupation factors of the two conformers at site 2 changed with varying temperature. The population of the minor conformer decreased to be negligible on lowering the temperature.

3.1.3. *Molecular motion responsible for the disorder.* The dynamic disorder is attributed to the torsional vibration of the N—Ph bonds, during which the two benzene rings remain parallel with each other (Fig. 5). In the course of the vibration the orientations of the benzene rings to the crystal lattice do not change, but those of the N=N moieties do (Fig. 5b). The same type of vibration, which causes an apparent shrinkage of the central bonds, has been reported to occur in the crystals of (E)-stilbenes and 1,2-diphenylethanes (Ogawa, Sano, Yoshimura, Takeuchi & Toriumi, 1992; Harada, Ogawa & Tomoda, 1995). When the vibration takes place with a much larger amplitude, a molecule with one of two orientations, conformer A (Fig. 5a), could change into the conformer with the other orientation, conformer B (Fig. 5d), through the conformation in which the azo unit (C—N=N—C) is perpendicular to the benzene rings (Fig. 5c). Thus, the conformational interconversion between conformers A and B takes place in crystals. The populations of the two conformers would show the temperature dependence if the two conformers have different stabilities in crystals. The dynamic disorder at site 2 is, therefore, ascribed to the
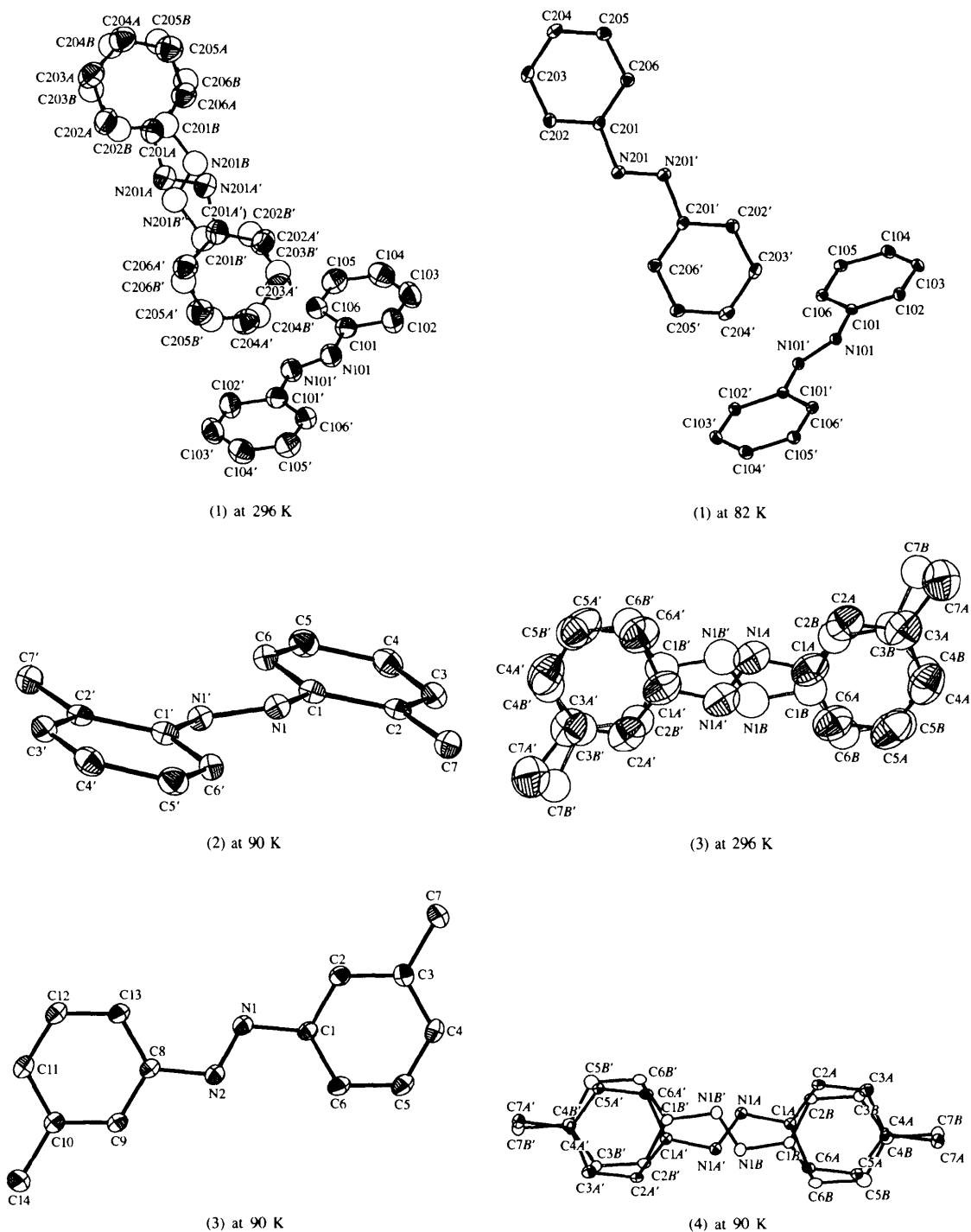
(1) at 296 K

(1) at 82 K

(2) at 90 K

(3) at 296 K

(3) at 90 K

(4) at 90 K

Fig. 3. Perspective views of the (E)-azobenzenes (1)–(4) with the atom numbering scheme. The ellipsoids are drawn at the 50% probability level.

conformational interconversion through the torsional vibration of the N—Ph bonds. It is to be noted that a similar picture for the molecular motion has been suggested by Ueda and his coworkers without any information on the temperature dependence of the crystal structures (Ueda, Nakamura & Chihara, 1988).

3.1.4. *Apparent shrinkage of the N=N bond.* Although there is no indication of disorder at site 1, the structure of molecule 1 has anomalous features (Table 3). The structure has so far been regarded and often used as the standard experimental structure of azobenzenes. The availability of the accurate structure

Table 2. *Fractional atomic coordinates and equivalent isotropic displacement parameters ($\mathring{A}^2$) (1)–(4)*

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

	x	y	z	U_{eq}
(1) at 296 K (non-disordered model)				
N101	0.0031 (2)	−0.1023 (4)	−0.5118 (2)	0.0448 (7)
C101	0.0737 (2)	−0.1341 (4)	−0.5674 (2)	0.0397 (7)
C102	0.0595 (3)	−0.3446 (5)	−0.6144 (2)	0.0520 (8)
C103	0.1228 (3)	−0.3894 (6)	−0.6707 (2)	0.0560 (9)
C104	0.2029 (3)	−0.2293 (6)	−0.6780 (2)	0.0553 (9)
C105	0.2187 (3)	−0.0227 (6)	−0.6287 (2)	0.0524 (8)
C106	0.1541 (2)	0.0273 (5)	−0.5741 (2)	0.0437 (8)
N201	−0.4802 (3)	0.0753 (5)	−0.9718 (2)	0.0723 (9)
C201	−0.3511 (3)	0.0467 (6)	−0.9213 (2)	0.0557 (9)
C202	−0.2990 (3)	0.2296 (7)	−0.8614 (3)	0.0664 (10)
C203	−0.1791 (3)	0.2308 (7)	−0.8099 (2)	0.0687 (11)
C204	−0.1100 (3)	0.0516 (7)	−0.8169 (2)	0.0668 (10)
C205	−0.1604 (4)	−0.1315 (7)	−0.8757 (3)	0.0688 (11)
C206	−0.2810 (3)	−0.1356 (6)	−0.9281 (2)	0.0633 (10)
(1) at 296 K (disordered model)				
N101	0.0035 (2)	−0.1022 (4)	−0.5116 (2)	0.0454 (6)
C101	0.0735 (2)	−0.1341 (4)	−0.5674 (2)	0.0398 (7)
C102	0.0597 (3)	−0.3441 (5)	−0.6143 (2)	0.0514 (8)
C103	0.1225 (3)	−0.3892 (5)	−0.6709 (2)	0.0570 (8)
C104	0.2026 (3)	−0.2292 (5)	−0.6781 (2)	0.0549 (8)
C105	0.2188 (2)	−0.0226 (5)	−0.6287 (2)	0.0529 (8)
C106	0.1541 (2)	0.0277 (4)	−0.5740 (2)	0.0439 (7)
N201A	−0.4773 (2)	0.0756 (5)	−0.9695 (2)	0.0543 (8)
C201A	−0.35277 (14)	0.0548 (5)	−0.9205 (2)	0.0476 (9)
C202A	−0.2966 (2)	0.2370 (4)	−0.8594 (2)	0.0584 (11)
C203A	−0.1739 (2)	0.2303 (5)	−0.8075 (2)	0.0625 (12)
C204A	−0.10728 (15)	0.0414 (6)	−0.8168 (3)	0.0599 (12)
C205A	−0.1634 (2)	−0.1408 (5)	−0.8778 (3)	0.0631 (12)
C206A	−0.2862 (2)	−0.1341 (4)	−0.9297 (2)	0.0555 (10)
N201B	−0.4619 (6)	−0.0768 (16)	−0.9940 (9)	0.055 (3)
C201B	−0.3469 (6)	−0.0145 (25)	−0.9294 (12)	0.055 (3)
C202B	−0.3250 (12)	0.1949 (23)	−0.8797 (12)	0.055 (3)
C203B	−0.2088 (15)	0.2557 (24)	−0.8212 (13)	0.055 (3)
C204B	−0.1145 (10)	0.1072 (29)	−0.8124 (14)	0.055 (3)
C205B	−0.1364 (6)	−0.1022 (27)	−0.8622 (15)	0.055 (3)
C206B	−0.2526 (8)	−0.1630 (23)	−0.9207 (13)	0.055 (3)
(1) at 82 K				
N101	0.00539 (9)	−0.1060 (2)	−0.50960 (7)	0.0111 (2)
C101	0.07586 (9)	−0.1389 (2)	−0.56691 (8)	0.0102 (2)
C102	0.06186 (10)	−0.3545 (2)	−0.61418 (8)	0.0124 (2)
C103	0.12675 (11)	−0.4004 (2)	−0.67205 (8)	0.0141 (2)
C104	0.20854 (11)	−0.2357 (2)	−0.67948 (8)	0.0141 (2)
C105	0.22447 (10)	−0.0233 (2)	−0.62940 (8)	0.0131 (2)
C106	0.15803 (10)	0.0270 (2)	−0.57358 (8)	0.0111 (2)
N201	−0.47643 (9)	0.0740 (2)	−0.96733 (7)	0.0146 (2)
C201	−0.34910 (10)	0.0484 (2)	−0.91860 (8)	0.0125 (2)
C202	−0.29189 (11)	0.2326 (2)	−0.85654 (9)	0.0148 (2)
C203	−0.16799 (11)	0.2263 (2)	−0.80606 (9)	0.0165 (2)
C204	−0.10181 (11)	0.0349 (2)	−0.81629 (9)	0.0162 (2)
C205	−0.15948 (11)	−0.1495 (2)	−0.87794 (8)	0.0157 (2)
C206	−0.28305 (11)	−0.1442 (2)	−0.92981 (8)	0.0142 (2)
(2) at 296 K				
N1	0.77696 (9)	0.8060 (2)	0.52862 (9)	0.0551 (5)
C1	0.72483 (11)	0.9597 (2)	0.57772 (10)	0.0506 (5)
C2	0.78106 (12)	1.1281 (3)	0.61859 (11)	0.0541 (5)
C3	0.7323 (2)	1.2800 (3)	0.66668 (13)	0.0669 (6)
C4	0.6330 (2)	1.2636 (4)	0.67515 (15)	0.0740 (6)
C5	0.57937 (13)	1.0942 (4)	0.63658 (14)	0.0711 (6)
C6	0.62490 (12)	0.9429 (3)	0.58761 (12)	0.0599 (6)
C7	0.88921 (14)	1.1480 (4)	0.6097 (2)	0.0713 (6)
(2) at 90 K				
N1	0.77756 (8)	0.8038 (2)	0.53181 (8)	0.0192 (4)
C1	0.72436 (10)	0.9615 (2)	0.57945 (9)	0.0178 (4)
C2	0.78083 (10)	1.1345 (2)	0.62087 (9)	0.0185 (4)
C3	0.73153 (10)	1.2914 (2)	0.66758 (10)	0.0210 (4)
C4	0.63025 (10)	1.2747 (2)	0.67543 (10)	0.0229 (4)

Table 2 (*cont.*)

	x	y	z	U_{eq}
C5	0.57577 (11)	1.0988 (2)	0.63632 (10)	0.0224 (4)
C6	0.62257 (10)	0.9423 (2)	0.58837 (9)	0.0198 (4)
C7	0.89086 (10)	1.1549 (2)	0.61286 (11)	0.0224 (4)
(3) at 296 K (non-disordered model)				
N1	0.04122 (13)	1.0169 (2)	0.5118 (2)	0.0800 (6)
C1	0.1142 (2)	0.9339 (2)	0.4620 (3)	0.0710 (6)
C2	0.2083 (2)	0.9659 (2)	0.4972 (3)	0.0748 (6)
C3	0.2851 (2)	0.8961 (2)	0.4584 (3)	0.0771 (7)
C4	0.2656 (2)	0.7923 (2)	0.3812 (3)	0.0836 (7)
C5	0.1726 (2)	0.7594 (2)	0.3448 (3)	0.0920 (8)
C6	0.0953 (2)	0.8297 (2)	0.3847 (3)	0.0822 (7)
C7	0.3871 (2)	0.9313 (4)	0.4983 (6)	0.1081 (10)
(3) at 296 K (disordered model)				
N1A	0.0423 (2)	1.0165 (2)	0.5117 (4)	0.0729 (8)
C1A	0.11393 (14)	0.9363 (2)	0.4624 (3)	0.0679 (9)
C2A	0.2095 (2)	0.96854 (13)	0.4982 (3)	0.0720 (9)
C3A	0.28574 (12)	0.8948 (2)	0.4583 (3)	0.0768 (10)
C4A	0.2665 (2)	0.7887 (2)	0.3825 (3)	0.0822 (11)
C5A	0.1710 (2)	0.75650 (14)	0.3467 (4)	0.0887 (11)
C6A	0.09468 (14)	0.8303 (2)	0.3867 (3)	0.0808 (10)
C7A	0.38880 (14)	0.9295 (3)	0.4969 (5)	0.1004 (13)
N1B	−0.0001 (8)	0.9500 (11)	0.4746 (49)	0.076 (11)
C1B	0.0954 (12)	0.9019 (17)	0.4619 (39)	0.063 (6)
C2B	0.1811 (14)	0.9538 (17)	0.5191 (37)	0.063 (6)
C3B	0.2707 (12)	0.9116 (18)	0.4627 (32)	0.063 (6)
C4B	0.2746 (12)	0.8176 (21)	0.3492 (38)	0.063 (6)
C5B	0.1890 (14)	0.7657 (20)	0.2920 (41)	0.063 (6)
C6B	0.0994 (12)	0.8079 (16)	0.3484 (38)	0.063 (6)
C7B	0.3631 (14)	0.9676 (27)	0.5243 (49)	0.063 (6)
(3) at 200 K				
N1	0.04227 (14)	1.0171 (2)	0.5106 (2)	0.0484 (7)
C1	0.1148 (2)	0.9348 (2)	0.4629 (3)	0.0450 (7)
C2	0.2097 (2)	0.9676 (2)	0.4986 (3)	0.0458 (8)
C3	0.2867 (2)	0.8957 (2)	0.4607 (3)	0.0487 (8)
C4	0.2662 (2)	0.7903 (2)	0.3848 (3)	0.0539 (8)
C5	0.1721 (2)	0.7571 (2)	0.3488 (3)	0.0571 (8)
C6	0.0954 (2)	0.8286 (2)	0.3865 (3)	0.0519 (8)
C7	0.3887 (2)	0.9312 (3)	0.4990 (5)	0.0664 (10)
(3) at 90 K				
N1	0.76656 (12)	0.28328 (11)	0.2426 (2)	0.0202 (3)
N2	0.73064 (12)	0.19796 (11)	0.2627 (2)	0.0196 (3)
C1	0.68386 (14)	0.35612 (12)	0.2873 (3)	0.0185 (3)
C2	0.7199 (2)	0.45098 (12)	0.2568 (3)	0.0194 (3)
C3	0.6472 (2)	0.52883 (13)	0.2945 (3)	0.0206 (3)
C4	0.5385 (2)	0.50924 (14)	0.3649 (3)	0.0231 (4)
C5	0.5029 (2)	0.41477 (15)	0.3960 (3)	0.0239 (4)
C6	0.5746 (2)	0.33712 (13)	0.3581 (3)	0.0213 (3)
C7	0.6862 (2)	0.63115 (13)	0.2609 (3)	0.0270 (4)
C8	0.81344 (14)	0.12575 (12)	0.2162 (3)	0.0182 (3)
C9	0.78066 (15)	0.03067 (12)	0.2560 (3)	0.0187 (3)
C10	0.8542 (2)	−0.04664 (12)	0.2182 (3)	0.0193 (3)
C11	0.9609 (2)	−0.02640 (14)	0.1384 (3)	0.0219 (3)
C12	0.9931 (2)	0.06853 (15)	0.0978 (3)	0.0232 (4)
C13	0.9201 (2)	0.14506 (13)	0.1358 (3)	0.0209 (3)
C14	0.8200 (2)	−0.14905 (13)	0.2603 (3)	0.0267 (4)
(4) at 296 K				
N1A	0.0480 (2)	−0.4492 (6)	0.9988 (3)	0.0362 (6)
C1A	0.0654 (2)	−0.2449 (6)	0.8953 (3)	0.0300 (7)
C2A	0.1739 (2)	−0.1384 (9)	0.8868 (4)	0.0379 (9)
C3A	0.2003 (3)	0.0602 (10)	0.7872 (5)	0.0437 (12)
C4A	0.1182 (4)	0.1523 (8)	0.6961 (4)	0.034 (2)
C5A	0.0097 (3)	0.0459 (9)	0.7046 (4)	0.0343 (8)
C6A	−0.0167 (2)	−0.1527 (8)	0.8042 (4)	0.0345 (9)
C7A	0.1467 (6)	0.3666 (12)	0.5887 (6)	0.051 (2)
N1B	−0.0310 (3)	−0.4439 (7)	0.9566 (3)	0.0385 (7)
C1B	0.0234 (3)	−0.2399 (7)	0.8730 (3)	0.0309 (8)
C2B	0.1353 (3)	−0.1602 (10)	0.8841 (4)	0.0338 (10)
C3B	0.1796 (3)	0.0371 (11)	0.7938 (5)	0.0347 (10)
C4B	0.1120 (5)	0.1547 (10)	0.6925 (4)	0.040 (3)

Table 2 (cont.)

	x	y	z	U_{eq}
C5B	0.0001 (4)	0.0749 (12)	0.6814 (5)	0.0478 (15)
C6B	−0.0442 (3)	−0.1224 (11)	0.7716 (4)	0.0382 (10)
C7B	0.1598 (7)	0.3675 (15)	0.5951 (7)	0.044 (2)
(4) at 90 K				
N1A	0.04893 (10)	−0.4469 (3)	0.99932 (13)	0.0118 (2)
C1A	0.06517 (10)	−0.2382 (2)	0.89354 (11)	0.0105 (3)
C2A	0.17497 (9)	−0.1295 (4)	0.8856 (2)	0.0124 (3)
C3A	0.20168 (13)	0.0713 (5)	0.7846 (2)	0.0141 (4)
C4A	0.1186 (2)	0.1634 (5)	0.6916 (2)	0.0091 (8)
C5A	0.0088 (2)	0.0547 (4)	0.6996 (2)	0.0115 (3)
C6A	−0.01790 (9)	−0.1461 (3)	0.80052 (15)	0.0118 (3)
C7A	0.1474 (3)	0.3799 (8)	0.5827 (4)	0.0137 (5)
N1B	−0.03170 (14)	−0.4424 (4)	0.9557 (2)	0.0123 (3)
C1B	0.02333 (14)	−0.2348 (3)	0.87152 (15)	0.0106 (3)
C2B	0.13708 (13)	−0.1566 (4)	0.8828 (2)	0.0114 (4)
C3B	0.1823 (2)	0.0438 (7)	0.7921 (3)	0.0108 (4)
C4B	0.1138 (3)	0.1660 (8)	0.6901 (4)	0.0148 (14)
C5B	0.0000 (2)	0.0878 (7)	0.6789 (3)	0.0173 (5)
C6B	−0.04522 (14)	−0.1126 (5)	0.7695 (2)	0.0133 (4)
C7B	0.1625 (4)	0.3821 (12)	0.5923 (6)	0.0145 (7)

of molecule 1 is, therefore, of importance. The N=N bond in azobenzene, which is conjugated with two phenyl rings, is expected to be longer than that of diazene (HN=NH). The N=N bond length in diazene was reported to be 1.252 (2) Å (Carlotti, Johns & Trombetti, 1974). The length in molecule 1 at room temperature [1.249 (4) Å] is, however, not longer, but slightly shorter than that in diazene. The observed bond length increased with lowering the temperature. The torsion angle ω also showed a strong temperature dependence. Other geometrical parameters were almost unchanged with variation in temperature.

A similar phenomenon was commonly observed for the crystals of (E)-stilbenes and successfully explained in terms of the torsional vibration of the C—Ph bonds in crystals (Ogawa, Sano, Yoshimura, Takeuchi & Toriumi, 1992; Ogawa, Harada & Tomoda, 1995). In molecule 1 the same type of torsional vibration as the N—Ph bonds occurs at room temperature and the observed length of the N=N bond becomes apparently shorter than the true length. With lowering the temperature, the amplitude of the vibration becomes smaller. The apparent shrinkage becomes negligible and the true length of the bond becomes observed. The temperature dependence of the torsion angles can also be explained in terms of the anharmonicity in the potential describing the torsional vibration of the
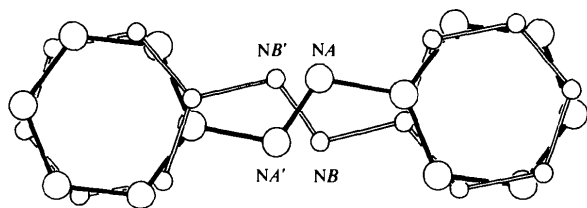
N—Ph bonds. The length of the N=N bond at 82 K [1.259 (2) Å] is in good accordance with that obtained from the DFT calculations (1.261 Å) and safely regarded as the standard length of the N=N bond in azobenzenes.

3.1.5. *Similarities and differences in molecular motion between two sites.* Comparison of the structures and their temperature dependence of molecules 1 and 2 reveals the difference in the extent of thermal motions in these molecules. In molecule 1 the vibration of the N—Ph bonds causes an apparent shrinkage of the N=N bond, but the structure of the molecule is restricted to only one conformation. The vibration almost ceases at 82 K and the shrinkage becomes negligible. In molecule 2, however, the same type of vibration occurs more vigorously than in molecule 1, leading to the conformational interconversion, which is the origin of the dynamic disorder at site 2. The disorder disappears at 82 K, but the amplitude of the vibration remains large enough to cause the shrinkage

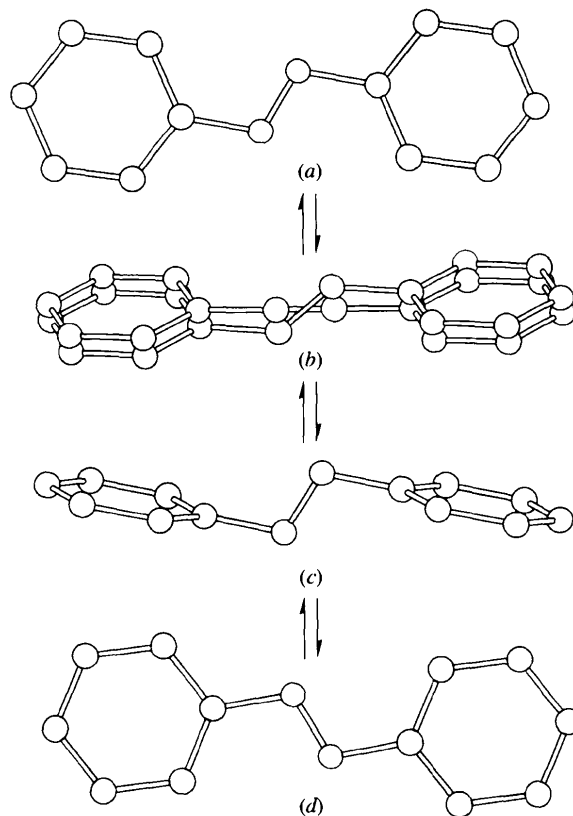Fig. 4. Orientational disorder observed for (1).

Fig. 5. Illustrations of the intramolecular motion and conformational interconversion in the crystals of (1). (a) View of a molecule with one of two orientations, conformer A. (b) Superimposed view of two molecules in the course of interconversion by the torsional vibration of the N—Ph bonds, during which the two benzene rings remain parallel to each other. (c) View of a transient conformation in the conformational inverconversion. (d) View of a molecule with the other orientation, conformer B.

Table 3. *Selected geometrical parameters for* (1)-(4)*

Compound	Origin	Temperature T (K)		Distance d_0 (Å)	Distance d_1, d_2 (Å)	Bond angle θ_1, θ_2 (°)	Torsion angle ω_1, ω_2 (°)
(1)	X-ray	296†	Molecule 1	1.249 (4)	1.431 (4)	114.1 (3)	±16.8 (4)
			Molecule 2‡	1.189 (6)	1.473 (4)	110.7 (4)	±5.5 (5)
		82†	Molecule 1	1.259 (2)	1.431 (1)	113.5 (1)	±21.0 (2)
			Molecule 2	1.251 (2)	1.431 (2)	114.1 (1)	±10.1 (2)
	DFT§			1.261	1.419	114.8	±0.1
(2)	X-ray	296†		1.240 (2)	1.431 (2)	114.2 (2)	±20.9 (3)
		90†		1.256 (2)	1.432 (2)	113.7 (1)	±26.0 (2)
	DFT§			1.262	1.417	115.2	±0.1
(3)	X-ray	296†‡		1.220 (3)	1.456 (3)	112.9 (2)	±4.1 (3)
		200†		1.246 (4)	1.436 (3)	114.0 (2)	±4.7 (4)
		90		1.260 (2)	1.431 (2)	114.1 (1)	3.8 (3)
					1.428 (2)	113.7 (1)	−7.0 (3)
(4)	X-ray	296†¶		1.251 (4)	1.426 (4)	114.6 (4)	±1.8 (5)
				1.252 (5)	1.434 (4)	114.4 (5)	±1.1 (6)
		90†¶		1.263 (2)	1.436 (2)	114.1 (2)	±2.0 (2)
				1.262 (3)	1.435 (2)	114.4 (2)	±0.5 (3)

* Definition of the geometrical parameters is given in Fig. 1.   † As the molecule is centrosymmetric, $d_1 = d_2$, $\theta_1 = \theta_2$ and $\omega_1 = -\omega_2$.   ‡ Non-disordered model.   § The geometry was optimized at the Becke 3LYP/6-31G* (DFT) level.   ¶ The geometrical parameters were obtained from the refinement under restrictions.

of the N=N bond [1.251 (2) Å]. A much lower temperature would be needed in order to cease the vibration and to observe the true length of the N=N bond in molecule 2.

3.2. Crystal structure of (E)-2,2'-dimethylazobenzene (2)

Crystal structural analysis of (2) was carried out at room temperature and 90 K. A phase transition was not observed between these temperatures. The molecule lies at an inversion center and the two phenyl rings are parallel to each other. No disorder was detected. The indications of the torsional vibration, however, appeared in the crystal structures. The length of the N=N bond, which apparently shrinks at room temperature [1.240 (2) Å], becomes longer at 90 K [1.256 (2) Å] and close to that obtained from the DFT calculations (1.262 Å). The torsion angle ω also shows a significant temperature dependence.

3.3. Crystal structure of (E)-3,3'-dimethylazobenzene (3)

The crystal structural analysis of (3) was carried out at room temperature, 200 and 90 K. A phase transition occurred between 200 and 90 K. The space group changed from *Pbca* (high-temperature phase) to $P2_12_12_1$ (low-temperature phase). The lattice parameters showed no drastic change around the transition point. With lowering the temperature, only the extinction rules derived from the symmetry of glide planes gradually faded at 170–140 K. This phenomenon would correspond to the phase transition at ~120 K reported from the measurement of solid-state ^{1}H NMR

spin-lattice relaxation time (Ueda, Nakamura & Chihara, 1988).

3.3.1. *Structure of high-temperature phase.* The structure analysis of (3) at room temperature was carried out. The molecule lies at an inversion center and the two phenyl rings are parallel to each other. The observed structure shows some features indicative of the same type of disorder as detected in (1) (Table 3). However, the disorder could not be resolved using the usual refinement and difference Fourier synthesis. To refine the structure with a disordered model, atomic coordinates of disordered molecules 2 of (1) were used as the initial geometry. Methyl C atoms were placed 1.51 Å apart from their carrier atoms. Refinement with some restraints was carried out. The degree of misorientation was determined to be 8 (1)%.

In the structure of (3) at 200 K disorder was hardly detected. The length of the N—Ph bond [1.436 (3) Å] is only marginally longer than the expected value (1.43 Å). The refinement using the disordered model was not successful, *i.e.* the site occupation factor of the misorientated molecule decreased to zero during the refinement. The disorder, which disappeared with lowering the temperature, is therefore proved to be the dynamic one that is caused by the conformational interconversion through the torsional vibration of the N—Ph bonds in crystals. The shrinkage of the N=N bond [1.246 (4) Å] indicates the occurrence of the torsional vibration with a moderate amplitude at 200 K.

3.3.2. *Structure of low-temperature phase.* The crystal structure of (3) at 90 K is significantly different from that at the high-temperature phase. The molecule loses crystallographic inversion symmetry. The two phenyl rings are not parallel to each other. The signs of the two torsion angles ω_1 and ω_2 are opposite, as in the

high-temperature phase, but the absolute values are not identical. No disorder was detected. The length of the N=N bond increases to the value 1.260 (2) Å. This observation shows that the torsional vibration which occurs at the high-temperature phase ceases at 90 K and that the apparent shrinkage of the N=N bond becomes negligible.

3.4. Crystal structure of (E)-4,4'-dimethylazobenzene (4)

The crystal structure of (4) was redetermined at different temperatures. The structure at room temperature is identical to that reported in the literature [monoclinic unit cell, $P2_1/a$, with $Z = 2$ (Padmanabhan, Shankar & Khubchandani, 1958; Brown, 1966b)]. The molecule lies at an inversion center and is orientationally disordered. Brown carried out the refinement on the assumption that the site occupation factors of the two conformers are equal to each other (Brown, 1966b). In order to determine whether the disorder is static or dynamic, refinement of the site occupation factors was performed.

The resolution of the disorder was much easier than those of (1) and (3), probably because of the high populations of both conformers. Direct methods and Fourier transformation resulted in the resolved peaks at four C atoms and the N atoms belonging to each conformer. The other C atoms in the benzene rings were fitted to regular hexagons. Methyl C atoms were placed 1.51 Å apart from their carrier atoms and refinement with some restraints was carried out. The ratio of the site occupation factors of the two conformers was determined to be 53.5 (6):46.5 (6) at room temperature and 57.8 (3):42.2 (3) at 90 K.

The dynamic nature of the disorder was deduced from a slight but distinct change in population with variation in temperature. Almost equal populations of the two conformers made their temperature dependence very weak and difficult to determine whether the disorder is dynamic or static. If the disorder is static, the ratio must remain constant at any temperature. If the disorder is dynamic, the ratio is dependent on the temperature and expected to be 52.4:47.6 at room temperature from the observed ratio at 90 K. This ratio is in fairly good accordance with the observed one. It is therefore safely concluded that the disorder is dynamic.

3.5. Disorder and molecular structure

As stated above, the disorder appears in the crystals of (1), (3) and (4), but not in (2). That is, while in the crystals of (1), (3) and (4) two conformers with different orientations coexist, in the crystals of (2) only one conformer exclusively exists. The reasons for the results are explained as follows.

The energies of two conformers of (1) and (4) are identical as free molecules, but different in crystals due
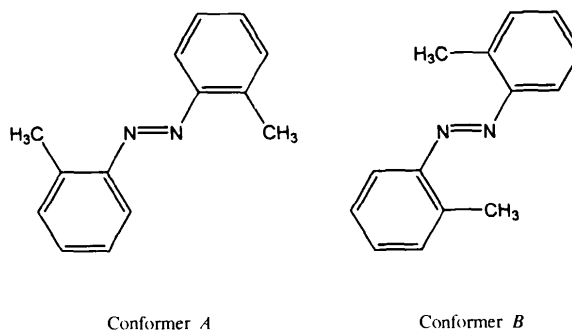

Fig. 6. Two conformers of (2).

to intermolecular interactions. The energy difference between the two conformers in (1) and (4) is, however, so small that both conformers exist in the crystals with small population differences. The energy difference calculated from the observed population ratio is ca 3.6 and 0.2 kJ mol⁻¹, respectively.

In contrast, the energies of two conformers of (2) are significantly different as free molecules, because intramolecular steric repulsion between the N atom and the methyl group of the distal benzene ring in one of two conformers (conformer B in Fig. 6) is much more severe than that between the N atom and the methyl group of the proximal benzene ring in the other conformer (conformer A in Fig. 6). The energy difference between two conformers was estimated to be 19 kJ mol⁻¹ as free molecules by the DFT calculations. Therefore, only the stable conformer is exclusively populated in crystals.

The lengths of the N=N bonds were calculated to be 1.261 Å for (1) and 1.262 Å for (2). The observed lengths of (1) (molecule 1), (2) and (3) at low temperature are in good accordance with the calculated values. The true length of the N=N bonds in azobenzenes is therefore safely estimated to be 1.26–1.27 Å.

4. Conclusions

From this study the following conclusions were drawn. An apparent shrinkage of the N=N bonds and its temperature dependence were observed in the crystal structures of (E)-azobenzenes and were interpreted in terms of an artifact caused by the torsional vibration of the N—Ph bonds in crystals. In (E)-azobenzene, (E)-3,3'-dimethylazobenzene and (E)-4,4'-dimethylazobenzene the amplitude of the vibration was large enough to cause conformational interconversion and consequently dynamic disorder in crystals. The absence of disorder in (E)-2,2'-dimethylazobenzene crystal was explained by the large difference in the energy of two conformers as free molecules. The true length of the N=N bond in (E)-azobenzenes was estimated to be 1.26–1.27 Å.

References

Altomare, A., Cascarano, G., Giacovazzo, C., Guagliardi, A., Burla, M. C., Polidori, G. & Camalli, M. (1994). *J. Appl. Cryst.* **27**, 435.

Becke, A. D. (1993). *J. Chem. Phys.* **98**, 5648–5652.

Bigelow, H. E. & Robinson, D. B. (1955). *Organic Synthesis,* Collective Vol. III, pp. 103–104. New York: John Wiley & Sons.

Bouwstra, J. A., Schouten, A. & Kroon, J. (1983). *Acta Cryst.* C39, 1121–1123.

Brown, C. J. (1966*a*). *Acta Cryst.* **21**, 146–152.

Brown, C. J. (1966*b*). *Acta Cryst.* **21**, 153–158.

Carlotti, M., Johns, J. W. C. & Trombetti, A. (1974). *Can. J. Phys.* **52**, 340–344.

Cosier, J. & Glazer, A. M. (1986). *J. Appl. Cryst.* **19**, 105–107.

Cruickshank, D. W. (1956). *Acta Cryst.* **9**, 754–756.

Dunitz, J. D. (1979). *X-ray Analysis and the Structure of Organic Molecules,* p. 248. Ithaca: Cornell University Press.

Dunitz, J. D., Maverick, E. F. & Trueblood, K. N. (1988). *Angew. Chem. Int. Ed. Engl.* **27**, 880–895.

Dunitz, J. D., Schomaker, V. & Trueblood, K. N. (1988). *J. Phys. Chem.* **92**, 856–867.

Eguchi, T., Kishita, M., Nakamura, N. & Chihara, H. (1988). *J. Phys. Soc. Jpn,* **57**, 4375–4378.

Eguchi, T., Mano, K. & Nakamura, N. (1989). *Z. Naturforsch. Teil. A,* **44**, 15–18.

Frisch, M. J., Trucks, G. W., Schlegel, H. B., Gill, P. M. W., Johnson, B. G., Robb, M. A., Cheeseman, J. R., Keith, T., Petersson, G. A., Montgomery, J. A., Raghavachari, K., Al-Laham, M. A., Zakrzewski, V. G.,

Ortiz, J. V., Foresman, J. B., Cioslowski, J., Stefanov, B. B., Nanayakkara, A., Challacombe, M., Peng, C. Y., Ayala, P. Y., Chen, W., Wong, M. W., Andres, J. L., Replogle, E. S., Gomperts, R., Martin, R. L., Fox, D. J., Binkley, J. S., DeFrees, D. J., Baker, J., Stewart, J. P., HeadGordon, M., Gonzalez, C. & Pople, J. A. (1995). *Gaussian94.* Revision D.3. Gaussian, Inc. Pittsburgh, USA.

Ghoshal, S. K., Sarkar, D. S. K. & Kastha, G. S. (1983). *Mol. Cryst. Liq. Cryst.* **91**, 1–24.

Hall, S. R., King, G. & Stewart, J. M. (1995). *Xtal3.4 Reference Manual.* University of Western Australia, Lamb, Perth, Australia.

Harada, J., Ogawa, K. & Tomoda, S. (1995). *J. Am. Chem. Soc.* **117**, 4476–4478.

Lange, J. J. de, Robertson, J. M. & Woodward, I. (1939). *Proc. R. Soc. (London) A,* **171**, 398–410.

Molecular Structure Corporation (1988). *MSC/AFC Diffractometer Control Software.* MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

Ogawa, K., Harada, J. & Tomoda, S. (1995). *Acta Cryst.* B51, 240–248.

Ogawa, K., Sano, T., Yoshimura, S., Takeuchi, Y. & Toriumi, K. (1992). *J. Am. Chem. Soc.* **114**, 1041–1051.

Padmanabhan, V. M., Shankar, J. & Khubchandani, P. G. (1958). *Proc. Indian Acad. Sci. Sect. A,* **47**, 323–328.

Saito, K., Yamamura, Y., Kikuchi, K. & Ikemoto, I. (1995). *J. Phys. Chem. Solids,* **56**, 849–857.

Sheldrick, G. M. (1985). *SHELXS86. Program for the Solution of Crystal Structures.* University of Göttingen, Germany.

Sheldrick, G. M. (1990). *Acta Cryst.* A46, 467–473.

Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.

Ueda, Y., Nakamura, N. & Chihara, H. (1988). *J. Phys. Soc. Jpn,* **57**, 4063–4064.