Temperature and Pressure Dependences of Thermal Cis-to-Trans Isomerization of Azobenzenes Which Evidence an Inversion Mechanism[1]

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Abstract: The mechanism of thermal cis-to-trans isomerization of azobenzene derivatives (rotation versus inversion) is discussed. *cis*-1 has an azobenzene covalently bridged to an aza crown ether, and rotation of the benzene rings is sterically restricted. The pressure dependence of the isomerization rate of *cis*-1 provided a ΔV^* of 2.0 mL mol^{-1}, indicating that the rotational mechanism which required an increase in the polarity at the transition state is not the case for *cis*-1. By using *cis*-1 as the standard azobenzene for the inversion mechanism it was demonstrated that the thermal isomerization of most cis azobenzenes occurs via an inversion mechanism, the activation parameters (ΔH^* and ΔS^*) including those of *cis*-1 being subject to a good ΔH^*–ΔS^* compensation relationship. The pressure effect also supported the inversion mechanism, the ΔV^* being too small (ca. −0.4 to −0.7 mL mol^{-1}) to consider the rotational mechanism. On the other hand, ΔH^*–ΔS^* plots for an azobenzene with push–pull substituents (e.g., 4-dimethylamino-4'-nitroazobenzene) deviated downward from a linear compensation relationship, and a negative, large ΔV^* (−22.1 mL mol^{-1}) resulted. Hence, the rotational mechanism may be operative for this azobenzene, the dipolar transition state being stabilized by the resonance power of these substituents. The fact that simple azobenzenes have small negative ΔV^* values and *cis*-1 has a small positive ΔV^* was rationalized in terms of void volume; that is, the crown ether ring is expanded in the inversion transition state. The explanation is well compatible with our previous finding that complexes K$^+$ and primary ammonium ions suppress the isomerization rate of *cis*-1. These results provide conclusive evidence for the inversion mechanism in most azobenzene derivatives and establish a new, unambiguous method to distinguish between the inversion and rotational mechanisms.

Introduction

Azobenzene derivatives exhibit photoinduced reversible cis–trans isomerism. The geometrical change between two isomers is so large that the phenomenon has been employed as a tool to enforce the conformational changes of cyclodextrins,[5] crown ethers,[6-8] polypeptide chains,[9] synthetic polymers,[10] and membranes.[11] However, the mechanism by which the cis–trans transformation takes place is not established unequivocally. In particular, the thermal cis-to-trans isomerization has been a controversial problem since two opposing mechanisms have been proposed: the reaction may proceed either via a rotational mechanism involving rotation about the N=N bond or an inversion mechanism involving flip–flop inversion of one of the nitrogen atoms.[12,13] The essential difference between the two mechanisms is that the rotational mechanism proceeds via a dipolar transition state accompanying a large volume change (Scheme I). Hence, the lack of major

solvent or pressure effects on the rate of isomerization may be cited as evidence against the rotational mechanism.

The rotational transition state can be either a singlet or triplet. However, relatively large preexponential factors preclude the latter possibility,[14] and the observed activation energies are too low to be explained by a singlet transition state. Theoretical calculations based on the CNDO/2 method predict activation energies for the rotational mechanism to be higher than 50 kcal/mol,[15,16] while experimental values are around 20 kcal/mol.[14,16,17] Thus, theoretical calculations support the inversion mechanism. Harberfield et al.[18] and Nishimura et al.[19] also argued for the inversion mechanism on the basis of the enthalpy of solvent transfer and substitutent effects, respectively. Whitten et al.[13] showed, however, that sizable kinetic solvent effects are observed for azobenzenes with push–pull substituents which would stabilize the dipolar rotational transition state. The finding suggests that the rotational mechanism is operative in these azobenzenes and that the energy-barrier difference between the two mechanisms is altered by substituent effects.

Despite these facts, Nerbonne and Weiss[17] supported the rotational mechanism for the isomerization of *cis*-azobenzene. Their proposal is based on the finding that the Arrhenius plot in a liquid crystal does not yield a single straight-line slope and the ΔS^* in the cholesteric phase is greater than that in the isotropic phase. Although "out-of-plane" rotational mechanism may be one way to explain the data, it certainly is not the only possibility. Their results may be compatible with the inversion mechanism if the planarity of the two phenyl rings changes during activation.

It seems to us that the confusion occurring in the preceding discussions stems from the fact that there is no definite standard,

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Table I. First-Order Rate Constants (k_1) for the Cis-to-Trans Thermal Isomerization in Various Solvents[a]

| compd no.	R_1	R_2	solvent	$k_1 \times 10^5$, s^{-1} at (°C)						
				15	20	30	40	50	55	60
1			benzene				1.56	4.16	5.84	9.64
1			methanol		0.190	0.470	1.11	2.46		
2	3-MC[b]	3-MC	benzene				0.628	1.73	3.36	5.36
2	3-MC	3-MC	o-DCB[c]				12.0	20.3		39.8
2	3-MC	3-MC	methanol		0.176		0.505	1.44		
3	4-MC	4-MC	o-DCB				4.58	9.22		15.8
3	4-MC	4-MC	methanol		0.157	0.477	1.35	3.60		
4	H	H	hexane		0.248	0.849	2.70			
4	H	H	chlorobenzene		1.80	5.95	18.2			
4	H	H	o-DCB	5.62	10.3	32.0	94.0			
5	4-NMe$_2$	4-NO$_2$	hexane	167	267	646	1480			
5	4-NMe$_2$	4-NO$_2$	benzene	836	1160	2220	4020			
5	4-NMe$_2$	4-NO$_2$	dioxane	583	970	2270	5400			
5	4-NMe$_2$	4-NO$_2$	benzene:dioxane (1:1 v/v)		842	1960	4420			

[a] Some of the rate constants have been reported in ref 1b and 6d, but they were redetermined under the identical reaction conditions (see Experimental Section). [b] MC = morpholinocarbonyl. [c] o-DCB = o-dichlorobenzene.

Table II. Thermodynamic Parameters for the Cis-to-Trans Thermal Isomerization in Various Solvents

compd no.	R_1	R_2	solvent	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, eu
1			benzene	18.2	-22.6
1			methanol	15.5	-31.9
2	3-MC[a]	3-MC	benzene	23.0	-9.3
2	3-MC	3-MC	o-DCB[b]	11.8	-39.0
2	3-MC	3-MC	methanol	19.8	-19.5
3	4-MC	4-MC	o-DCB	12.3	-39.3
3	4-MC	4-MC	methanol	19.1	-20.1
4	H	H	hexane	21.2	-12.0
4	H	H	chlorobenzene	20.5	-10.3
4	H	H	o-DCB[b]	19.6	-9.96
5	4-NMe$_2$	4-NO$_2$	hexane	15.0	-19.0
5	4-NMe$_2$	4-NO$_2$	benzene	10.7	-30.9
5	4-NMe$_2$	4-NO$_2$	dioxane	15.2	-15.8
5	4-NMe$_2$	4-NO$_2$	benzene:dioxane (1:1 v/v)	14.5	-18.5

[a] MC = morpholinocarbonyl. [b] o-DCB: o-dichlorobenzene.

Table III. First-Order Rate Constants ($k_1 \times 10^5$, s^{-1}) for the Thermal Cis-to-Trans Isomerization in Methanol

pressure, bar	1 (50 °C)	2 (55 °C)	4 (65 °C)
1	2.24 ± 0.02	1.44 ± 0.02	8.65 ± 0.06
300	2.16 ± 0.04	1.44 ± 0.02	
600	2.11 ± 0.02	1.45 ± 0.02	8.85 ± 0.16
900	2.06 ± 0.02	1.46 ± 0.02	
1200	2.00 ± 0.02	1.46 ± 0.04	8.95 ± 0.16
1500	1.97 ± 0.04	1.48 ± 0.04	
1800	1.95 ± 0.02	1.48 ± 0.03	9.12 ± 0.07
2100	1.91 ± 0.04	1.47 ± 0.03	9.09 ± 0.10

Table IV. $\Delta V^{\ddagger}$ in Various Solvents

compd no.	react temp °C	solvent	$\Delta V^{\ddagger}$, mL mol^{-1}
1	50	methanol	2.0
2	55	methanol	-0.4
4	65	methanol	-0.7
4	60	benzene	-1.2[a]
4	60	hexane	-3.3[a]
5	30	benzene	-22.1[a]
5	40	hexane	-0.7[a]

[a] Cited from ref 1a.

the isomerization mechanism being completely established. We recently synthesized an azobenzene-bridged crown ether (**1**).[6a,d]

trans-**1**

cis-**1**
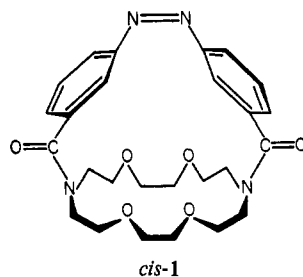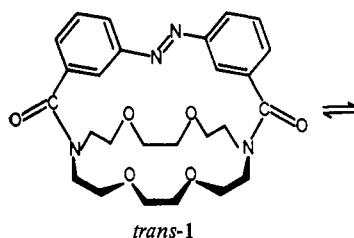
Since two benzene rings are covalently linked to the crown ether ring, the thermal cis-to-trans isomerization via the rotational mechanism is highly unlikely. The CPK model building suggests that the rotational transition state required either an extreme steric hindrance between the azobenzene and crown ether ring or a highly distorted conformation of the crown ether. On the other hand, the inversion of the azo linkage occurs smoothly without

requiring a significant steric distortion of the crown ether. It occurred to us that **1** would serve as a standard for the inversion mechanism. In this paper, we report a new, unambiguous method to distinguish between the rotational and the inversion mechanisms, with the aid of standard **1**.

Results

First-order rate constants for cis-to-trans thermal isomerization in various solvents are summarized in Table I. Based on the temperature dependence of these rate constants, we determined the activation parameters ($\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$) for **1** and several other azobenzene derivatives (**2**)–(**5**). The results are summaried in Table II.

2, $R_1 = R_2 =$ 3-CON⟨⟩O

3, $R_1 = R_2 =$ 4-CON⟨⟩O

4, $R_1 = R_2 =$ H
5, $R_1 =$ 4-NMe$_2$; $R_2 =$ 4-NO$_2$
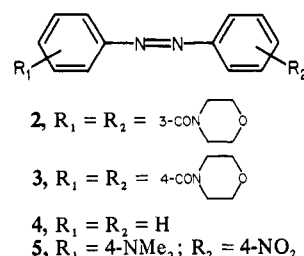
The pressure effects on the thermal cis-to-trans isomerization were examined in methanol for **1**, **2**, and **4**. The results are

Cis-to-Trans Isomerization of Azobenzenes
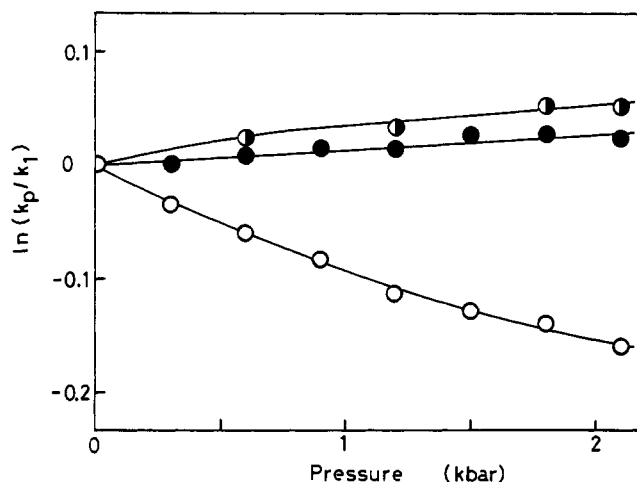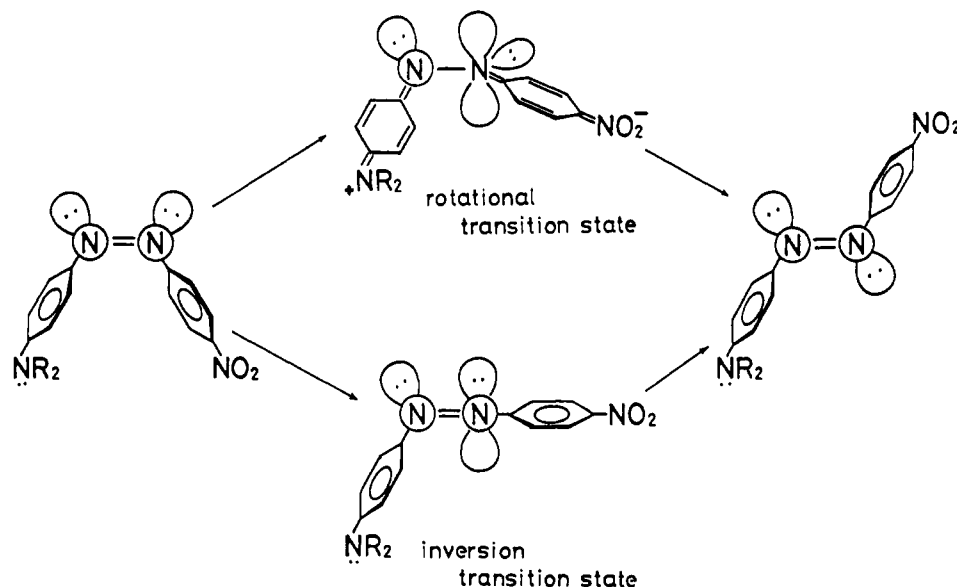
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Scheme I

Figure 1. Pressure effects on the first-order rate constants for cis-to-trans thermal isomerization: O, 1; ●, 2; ◐, 4.

summarized in Table III. In Figure 1, ln (k_p/k_1) $(k_p$ = first-order rate constant at p bar, k_1 = first-order rate constant at one bar) is plotted as a function of pressure. The ΔV^* values thus obtained are summarized in Table IV, together with those for 4 and 5 previously determined in benzene and hexane.[1a]

Discussion

In the first place, we have to corroborate whether **1** serves as a definite standard for the inversion mechanism. As mentioned in the Introduction, the CPK model of **1** suggests that the crown ether in the rotational transition state is highly distorted. It is presumed, therefore, that the rotational isomerization of *cis*-**1**, if it were possible, would proceed via an energetically unfavorable transition state, resulting in an extremely large free energy of activation. We observed, however, that *cis*-**1** is isomerized in the dark to *trans*-**1** quantitatively, and the first-order rate constant $(k_1 = 1.56 \times 10^{-5}$ s^{-1} at 40 °C in benzene) is comparable with that of an analogous azobenzene, 3,3'-bis(morpholinocarbonyl)-azobenzene (2) $(k_1 = 6.28 \times 10^{-6}$ s^{-1} at 40 °C in benzene). The result argues against the involvement of the rotational transition state.

More unequivocal evidence is derived from the pressure effect. It is now recognized that the activation volume obtained from the kinetic effect of pressure according to eq 1 is quite sensitive to the polarity change of the reactant(s) during activation.[20] For

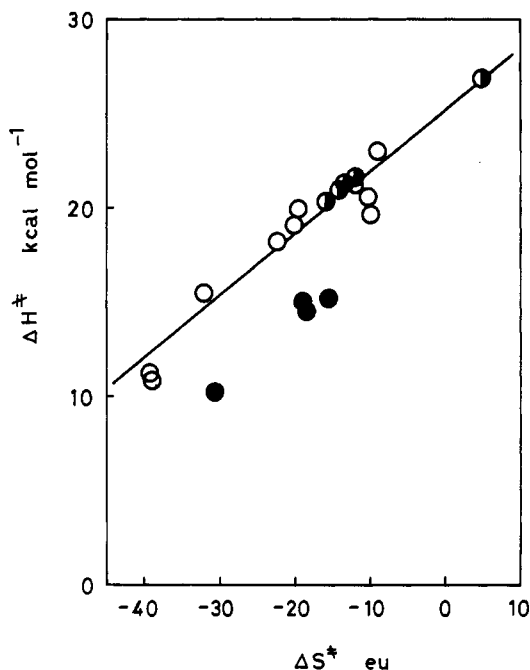$$\Delta V^* = -RT(\partial \ln k_1/\partial p)_T \qquad (1)$$

Figure 2. $\Delta H^*-\Delta S^*$ compensation relationship. O, 1–4 in various solvents (see Table II); ●, 5 in various solvents; ◐, cited from ref 17.

instance, one may expect a sizable rate acceleration by pressure ($\Delta V^* = -20$ to -10 mL mol^{-1}) for the rotational mechanism which occurs via the dipolar transition state (i.e., electrostriction). On the other hand, the pressure increase would cause little change in the reaction occurring via the inversion transition state, since the increase in the polarity is hardly expected. The ΔV^* of **1** in methanol being small enough (2.0 mL mol^{-1}: Table IV), the polarity cannot increase during the activation process of *cis*-**1**. One can conclude, therefore, that the thermal isomerization of *cis*-**1** occurs via the inversion mechanism.

Based on the foregoing lines of evidence, we can now regard **1** as a standard for the inversion mechanism. Interestingly, we found that the ΔH^* and ΔS^* values for **1–4** are subject to a compensation relationship (Figure 2). The plots are expressed by eq 2 with correlative coefficient r = 0.961. According to the

$$\Delta H^* \text{ (cal mol}^{-1}) = 306\Delta S^* \text{ (eu)} + 2.47 \times 10^4 \qquad (2)$$

(20) Asano, T.; le Noble, W. J. *Chem. Rev.* **1978**, *78*, 407.

concept proposed by Leffler,[21] the finding implies that the thermal isomerization of these azobenzenes occurs via a single mechanism. The entity of the $\Delta H^{\ast}$–$\Delta S^{\ast}$ compensation relationship has been reported for a series of substituted azobenzenes and for azobenzene in a series of different solvents.[19,22,23] The importance of the present finding resides in the fact that the plots for the standard (**1**) are essentially colinear with other plots for **2–4**. One can thus derive the second conclusion that the thermal isomerization of **2–4** also occurs via the inversion mechanism. The pressure effect on the thermal isomerization rate of **2** and **4** provided sufficiently small, negative $\Delta V^{\ast}$ values (Table IV). The results also support the inversion mechanism.

The behavior of **5** with push–pull substituents is more complicated, for the energy barrier between two mechanisms may be close to each other. One of the authors has found that the $\Delta V^{\ast}$ in hexane (-0.7 mL mol^{-1}) is comparable with those of **2** and **4**, whereas it decreased to -22.1 mL mol^{-1} in benzene.[1a] This suggests that the reaction mechanism changes (at least partially) from inversion in hexane to rotation in benzene. As reported by Whitten et al.,[13] the rate constants for **5** are very solvent dependent (Table II). We found that the plots of **5** in a $\Delta H^{\ast}$–$\Delta S^{\ast}$ map significantly deviate downward from the linear relationship (Figure 2). When the least-squares computation was performed including four plots for **5**, the correlation coefficient was as inferior as 0.777. The magnitude of the deviation from eq 2 is 4.5 kcal mol^{-1} in benzene, 4.5 kcal mol^{-1} in benzene–dioxane mixture (1:1 in vol), 4.7 kcal mol^{-1} in dioxane, and 3.9 kcal mol^{-1} in hexane. It is interesting that the larger deviation is seen for polar solvents. When considering the thermodynamic data together with the above pressure effect, one may safely derive the third conclusion that the deviation is due to the involvement of the rotational mechanism. The magnitude of the deviation would become a measure of the contribution of the rotational mechanism.

Here, a question arises as to what is reflected by a break point in the Arrhenius plot in the liquid crystal.[17] Although Nerbonne and Weiss[17] regarded the positive shift of the $\Delta S^{\ast}$ in the cholesteric phase as evidence for the rotational mechanism, the activation parameters obtained by them (half-filled circles in Figure 2) are completely included in the linear eq 2. Adding their data to ours, we obtained eq 3 ($r = 0.974$), which is essentially equivalent to

$$\Delta H^{\ast} \ (\text{cal mol}^{-1}) = 320 \Delta S^{\ast} \ (\text{eu}) + 2.51 \times 10^4 \qquad (3)$$

eq 2.[24] The break point probably reflects the influence of a phase transition of the liquid crystal on the inversion mechanism but not on the rotational mechanism.[25]

Examination of Table IV reveals that **2**, **4**, and **5** give negative $\Delta V^{\ast}$ values, while only **1** gives positive a $\Delta V^{\ast}$. The positive $\Delta V^{\ast}$ of 2.0 mL mol^{-1} may be rationalized in terms of void volume;[26] that is, when the cis-to-trans isomerization of the azobenzene bridge of **1** occurs in conjugation with the conformational change of the crown ether, it may induce the expansion of the inner space of the crown ether ring, into which solvent molecules cannot penetrate. Such effect cannot be expected for other simple azobenzene derivatives. The $\Delta V^{\ast}$ difference between **1** and other simple azobenzenes (ca. 2.5 mL mol^{-1}) is comparable with the inner void of cyclohexane.[26]

In the solvent extraction of alkali metal cations, it has been found that *cis*-**1** binds K$^+$ and Rb$^+$ preferably, whereas *trans*-**1**

binds Li$^+$, Na$^+$, and primary ammonium salts preferably.[6a,d] Hence, the ring size of *cis*-**1** is somewhat greater than that of *trans*-**1**. The rate of the thermal isomerization was suppressed by both K$^+$ and primary ammonium salts.[6d] The rate suppression by K$^+$ may be accounted for by the stabilization of the initial state due to the favorable complexation. However, this explanation is not valid for the rate suppression by primay ammonium ions, because they form more stable complexes with *trans*-**1** in the final state. We thus accomodated the rate suppression in terms of destabilization of the transition state and not in terms of difference between the initial state and the final state, and predicted that transformation from *cis*-**1** to *trans*-**1** proceeds via "some metastable transient conformation of the crown ether moiety".[6d] As seen in Scheme I, one of the nitrogens must employ a sp hybrid orbital in the inversion transition state, forming a straight N=N—C bond. The CPK model predicts that the distance between the 3 and 3′ position of the benzene rings becomes greatest at this transition state. Since the distance is transmitted to the crown ether via the covalent bonds, the crown ether ring is enforced to expand in the transition state and bears the void volume. This would become the origin of positive $\Delta V^{\ast}$. As a summary of these results, one may consider that the size of crown ether is in the order: inversiontransition state > *cis*-**1** > *trans*-**1**. To induce the

cis-1	inversion transition state	*trans*-1
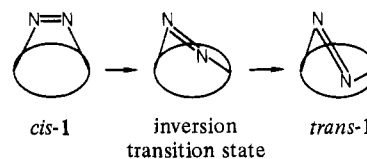
isomerization of the azobenzene bridge, the interaction between the crown ether and the complexed cation must be disrupted (or weakened) temporarily. This requires an additional free–energy of activation. This is our forth conclusion.

In conclusion, the present study established that (i) **1** serves as a standard azobenzene for the inversion mechanism, (ii) the thermal cis-to-trans isomerization of *cis*-azobenzenes without push–pull substituents occurs via the inversion mechanism, (iii) two mechanisms can be distinguished on the basis of a $\Delta H^{\ast}$–$\Delta S^{\ast}$ compensation relationship and pressure effects, and (iv) the thermal isomerization of *cis*-**1** induces the expansion of the crown ether at the transition state, which is reflected by the void volume and the rate suppression by K$^+$ and primary ammonium ions. These findings provide conclusive evidence for the inversion mechanism.

Experimental Section

Materials. Preparations of **1**, **2**, and **3** were described previously.[6d] **5** was prepared by diazo coupling from *N,N*-dimethylaniline and *p*-nitroaniline and recrystallized from chlorobenzene: mp 225–226.5 °C (lit.[27] 225–226 °C).

Photoisomerization and Kinetics. Photoisomerization of **1–4** was carried out with a 500-W high-pressure Hg lamp and that of **5** with a 150-W tungsten lamp. The details of the method are described previously.[6d] The rate of the thermal isomerization was followed spectrophotometrically. The rate of *cis*-**5** was very fast. Thus, a cuvette containing a solution of *trans*-**5** was put in a thermostated cell holder, and after equilibration to the desired temperature the solution was irradiated with a 150-W tungsten lamp. The cuvette was quickly transferred to the thermostated cell holder in a spectrophotometer (Hitachi 200), and the increase in the absorption band of *trans*-**5** (ca. 480 nm) was monitored as a function of time. Since the rate constants for **1–4** were suppressed by light from the spectrophotometer, we measured the absorbance for a few seconds per hour, and except for the measurement time, light from the spectrophotometer was shut down by a black plate. The absorbance plotted against time satisfied a first-order equation for at least 4 half-lives. Finally, we corroborated that the initial spectrum is regenerated after 1 day. The first-order rate constants thus determined were in accord with those determined by the sampling method within the experimental error (less than 3%).

The pressure effects for **5** were measured as described elsewhere.[1a,28] The rates of *cis*-azobenzene were measured by means of a sampling

(21) Leffler, L. E.; Grunwald, E. "Rates and Equilibria of Organic Reactions"; Wiley: New York, 1963; Chapter 9.

(22) Nishimura, N.; Sueishi, T.; Yamamoto, S. *Chem. Lett.* **1979**, 429.

(23) Wolf, E.; Cammenga, H. K. *Z. Phys. Chem.* **1977**, *107*, 21, and references cited therein.

(24) Five plots obtained by Nerbonne nd Weiss[17] also show a good linear relationship ($\Delta H^{\ast} = 317\Delta S^{\ast} + 2.54 \times 10^1$) with $r = 0.999$.

(25) In order to ascertain whether **1** provides a similar break point, we tried to determine the rate constants for the thermal isomerization of *cis*-**1** in the liquid crystal (35:65 w/w) mixture of cholesteryl chloride and cholesteryl nonanoate). However, the attempt ended in failure because of the poor solubility of **1** in the liquid-crystal phase.

(26) (a) Asano, T.; le Noble, W. J. *Rev. Phys. Chem. Jpn.* **1973**, *43*, 82; (b) Asano, T. *Ibid.* **1979**, *49*, 56, and references cited therein.

(27) Nölting, E. *Ber.* **1887**, *20*, 2994.

(28) Asano, T. *Rep. Fac. Eng. Oita Univ.* **1980**, *6*, 95.

technique.[29] The contact of methanol with Viton O-rings which were used to separate the reaction mixture from the pressurizing fluid caused an increase in absorption at the near-ultraviolet region. Therefore, the rates for **2** and **3** were obtained by the batch method. The reaction mixture was kept in a glass hypodermic syringe with a Teflon cap for 3 to 15 h at the desired conditions and analyzed spectrophotometrically.

Oxygen was not excluded during kinetic measurements. We determined the rate constants for azobenzene under anaerobic (N₂) conditions; they were in good agreement withe aerobic rate constants within experimental error.

(29) Whalley, E. *Adv. Phys. Org. Chem.* **1964**, *2*, 93.

Neutron and X-ray Diffraction Studies of Tris(methyldiphenylphosphine)[tetrahydroborato(1−)]copper, Cu[P(C₆H₅)₂CH₃]₃(BH₄). The First Accurate Characterization of an Unsupported Metal-Hydrogen-Boron Bridge Bond

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Abstract: A single-crystal neutron diffraction study of tris(methyldiphenylphosphine)[tetrahydroborato(1−)]copper, Cu-(PPh₂Me)₃(BH₄), has been carried out at low temperature (15 ● 0.5 K) in order to examine the nature of the unidentate attachment of the tetrahydroborate group to the Cu atom. The compound crystallizes in the space group *Pna*2₁, *Z* = 4. Cell constants at 15 K are *a* = 19.980 (2) Å, *b* = 10.175 (1) Å, and *c* = 17.282 (2) Å. The structure was refined on the basis of measured intensities of 4765 reflections, and final discrepancy factors for all reflections are $R(F^2)$ = 0.043 and $R(wF^2)$ = 0.047. One H atom of the tetrahydroborate group participates in bonding to the Cu atom with Cu–H = 1.697 (5) Å, Cu–B = 2.518 (3) Å, and Cu–H–B = 121.7 (4)°. There is no evidence for other Cu–H bonding interactions (the second shortest CuH distance is 2.722 (7) Å). The H–Cu–P angles [86.2 (2)°, 108.5 (2)°, 115.3 (2)°] are more widely distributed than the B–Cu–P angles [101.4 (6)°, 101.7 (7)°, 108.8 (7)°], and the bridging H atom is significantly displaced off the pseudothreefold axis defined by the CuP₃ group. This bent, off-center positioning of the bridging H atom is reminiscent of similar observations found in M–H–M bridges and may provide some information about the nature of M–H–B overlap. The tetrahydroborate group is somewhat distorted from tetrahedral symmetry; three of the four B–H distances agree well with one another (1.179 ● 0.005 Å), but the fourth [1.330 (6) Å] is significantly longer. Surprisingly, however, the long distance is not the one associated with the Cu–H–B bridge. In addition to the neutron diffraction analysis, structures were determined from room-temperature X-ray data obtained from two other crystals. In general, for nonhydrogen structural parameters there is good agreement among all of the determinations including the original work of Atwood et al. However, one outstanding point of disagreement occurs in the Cu–B distances which range from 2.498 (5) to 2.650 (5) Å in the individual determinations. This variation in distance may be indicative of disorder of the (*μ*-H)BH₃ unit.

For the past few years we[1a,e] have been investigating compounds having unsupported[2] metal–hydrogen–metal bonds with neutron diffraction techniques, in an attempt to understand the bonding patterns in three-center/two-electron (3c, 2e⁻) bonds.[3] The results

of these studies, and those of others,[4] led us to conclude that the overlap pattern in the M–H–M bridge bond is of the "closed" type[5] and also led us to suspect that the M–H–M bond is inherently bent. We have therefore sought to extend these studies to metal–hydrogen–boron systems (and, eventually, boron–hydrogen–boron systems), to see if these general conclusions also hold for other types of 3c, 2e⁻ bonds.

Unsupported[2] M–H–B bonds are very rare. The unidentate tetrahydroborate ligand is suspected to exist in a few cobalt,[6a]

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(2) We define a molecule having an unsupported 3c, 2e⁻ bond as one in which the two halves of the molecule are held together solely by one 3c, 2e⁻ bond, without other bridging groups. Thus, molecules such as B₂H₆ or H₂-Re₂(CO)₈, which have two X–H–X bridges, are not included by this definition. An unsupported Zr–H–Al bridge, incidentally, has been reported recently [Kopf, J.; Vollmer, H. J.; Kaminsky, W. *Cryst. Struct. Commun.* **1980**, *9*, 985].

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(5) A "closed" 3c, 2e⁻ bond is one in which all three orbitals overlap in a common region of space; in the case of the M–H–M bond this would mean that there is a significant amount of M–M bonding as well as M–H bonding.