reported above, a clean separation of unreacted substrate from products by trap-to-trap distillation was not possible. The organic reactant-product mixture was analyzed by VPC after removal of excess nitrous oxide.

Most VPC analysis was conducted on various columns of dinonylphthalate. Other VPC columns used were: 5A molecular sieves for noncondensable gases, saturated silver nitrate in benzyl cyanide for unreacted 1,4-cyclohexadiene, and propylene carbonate for purification and analysis of cyclobutene and bicyclobutane.

Product Identification. Major reaction products were identified by ir, NMR, and mass spectrometry and, when possible, by comparative VPC retention times. Minor reaction products (those formed in <7% yield) were identified by ir and mass spectrometry and by comparative VPC retention times. Isolated samples of product **17**, **19**, and **20** showed good correspondence to literature spectra.[13,27,28]

Spectra of *endo*-bicyclo[2.1.1]hexane-5-carboxaldehyde (**11**) are: high resolution mass of parent peak 110.0733 (obsd), 110.0731 (calcd); mass spectrum (70 eV) m/e 110 (I_R = 14), 109 (13), 95 (19), 92 (13), 91 (8), 81 (*100*), 79 (47), 66 (54); ir (thin film) 3002, 2915, 2802, 2705, 1735 cm^{-1}; NMR (C_3D_6O solvent) δ 0.88 (1 H, d, J = 6 Hz), 1.74 (3 H, s over m), 2.48 (1 H, m), 2.88 (2 H, m), 3.13 (2 H, m), 9.58 (1 H, d, $J \sim 1$ Hz).[29]

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Enthalpies of Solvent Transfer of the Transition States in the Cis–Trans Isomerization of Azo Compounds. The Rotation vs. the Nitrogen Inversion Mechanism

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Abstract: The enthalpies of transfer from cyclohexane to cyclohexanone of the reactants, transition states, and products in the cis-trans isomerization of *cis*-azobenzene and *cis-p*-chlorobenzenediazocyanide were determined calorimetrically. The relative magnitudes of these solvent transfer enthalpies suggest that the isomerization proceeds via a nitrogen inversion mechanism rather than via a rotational mechanism.

The remarkably facile cis-trans isomerization of compounds having an N=N bond[1-3] may proceed via a rotation about the N=N bond, or via inversion of one of the nitrogens (i.e., by way of an sp hybridized transition state).[4] The latter mechanism would account for the much greater ease of isomerization of azo compounds as compared with olefins, where the second mechanistic possibility does not exist.

One way to distinguish between these two possible transition states for this isomerization reaction is to consider the enthalpy of transfer of the transition state in this reaction from one solvent to another. We have shown[5] that this property, i.e., the enthalpy of transfer of the transition state from one solvent to another, δH^t, can provide useful information concerning the mechanism of a reaction. In particular, with the appropriate choice of solvents, this property, δH^t, may yield information concerning the geometry and the electronic constitution of the transition state. We report here a study on the cis-trans isomerization of azobenzene and p-chlorobenzenediazocyanide in a nonpolar solvent, cyclohexane, and in one having a substantial dipole, cyclohexanone (μ = 3 D[6]).

Results and Discussion

The enthalpy of transfer of a transition state from one solvent to another, δH^t, is obtained from the relation

$$\delta H^t = \delta \Delta H_s^r + \delta \Delta H^\ddagger$$

where $\delta \Delta H_s^r$ is the enthalpy of transfer of the reactants from one solvent to the other and $\delta \Delta H^\ddagger$ is the difference in the enthalpies of activation in the two solvents. To obtain

Table I. Heats of Solution,[a] ΔH_S, and Enthalpies of Transfer of Reactants from Cyclohexane to Cyclohexanone,[b] $\delta \Delta H_S{}^r$ (kcal/mol)

Compd	Solvent	$\Delta H_S{}^a$	$\delta \Delta H_S{}^{r\,b}$
cis-Azobenzene	Cyclohexane	6.42	−3.0
	Cyclohexanone	3.45	
cis-p-Chlorobenzene-diazocyanide	Cyclohexane	6.88	−4.0
	Cyclohexanone	2.92	

[a] Integral heat of solution, at concentrations of 0.003 to 0.01 *M*; standard deviations were less than 0.3 kcal/mol; temperature, 25°. [b] $\delta \Delta H_S{}^r = \Delta H_S(\text{cyclohexanone}) - \Delta H_S(\text{cyclohexane})$.

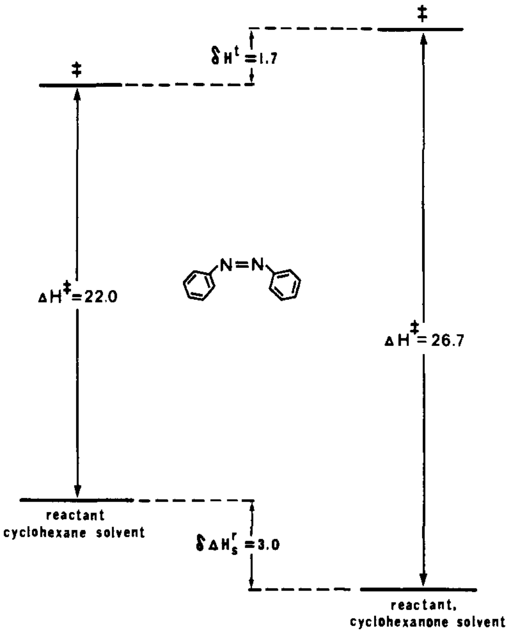

Figure 1. Relative enthalpies (kcal/mol) of the reactant and the transition state in the cis-trans isomerization of *cis*-azobenzene in cyclohexane and in cyclohexanone.

Table II. Enthalpies of Transfer, δH^t, from Cyclohexane to Cyclohexanone, of the Transition States in the Cis–Trans Isomerization of Azo Compounds (kcal/mol)

Compd	$\delta \Delta H_S{}^r$	$\delta \Delta H^{\ddagger a}$	$\delta H^{t\,b}$
cis-Azobenzene	−3.0	4.7	1.7
cis-p-Chlorobenzenediazocyanide	−4.0	4.2	0.2

[a] The difference in the activation enthalpies in the two solvents, $\delta \Delta H^\ddagger = \Delta H^\ddagger(\text{cyclohexanone}) - \Delta H^\ddagger(\text{cyclohexane})$, with the $\Delta H^\ddagger$ values taken from ref 1 and 2. [b] $\delta H^t = \delta \Delta H_S{}^r + \delta \Delta H^\ddagger$.

Table III. Heats of Solution,[a] ΔH_S, and Enthalpies of Transfer of Products from Cyclohexane to Cyclohexanone,[b] $\delta \Delta H_S{}^p$ (kcal/mol)

Compd	Solvent	$\Delta H_S{}^a$	$\delta \Delta H_S{}^p$
trans-Azobenzene	Cyclohexane	6.31	−1.96
	Cyclohexanone	4.35	
trans-p-Chlorobenzene-diazocyanide	Cyclohexane	7.60	−2.94
	Cyclohexanone	4.66	

[a] Integral heats of solution, at concentrations of 0.003 to 0.001 *M*; standard deviations were less than 0.3 kcal/mol; temperature, 25°. [b] $\delta \Delta H_S{}^p = \Delta H_S(\text{cyclohexanone}) - \Delta H_S(\text{cyclohexane})$.

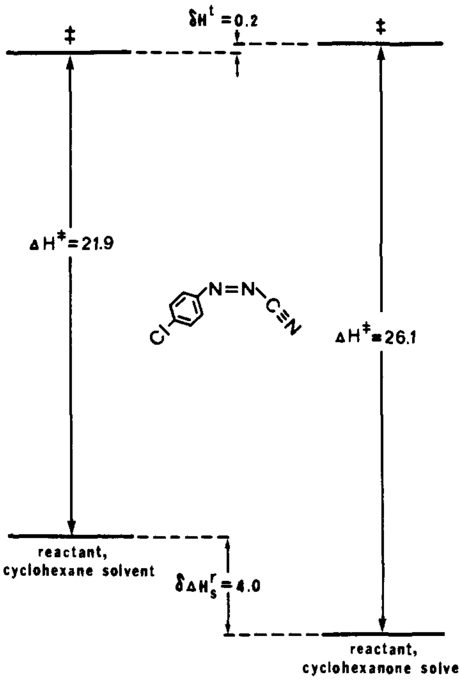

Figure 2. Relative enthalpies (kcal/mol) of the reactant and the transition state in the cis-trans isomerization of *cis*-4-chlorobenzenediazocyanide in cyclohexane and in cyclohexanone.

the enthalpies of transfer of our two reactants, *cis*-azobenzene and *cis-p*-chlorobenzenediazocyanide, we measured their heats of solution in the two solvents of interest. The results are shown in Table I. The enthalpies of transfer of the reactants, $\delta\Delta H_s{}^r$, and transition states, δH^t, are listed in Table II and are shown graphically in Figures 1 and 2.

Considering the case of azobenzene first, we see that although the enthalpy of transfer of the dipolar molecule *cis*-azobenzene (μ = 3 D[6]) from the nonpolar to the dipolar solvent is quite exothermic, the *enthalpy of transfer of the transition state is endothermic.* (See Figure 1.)

Since dipole-dipole interactions are undoubtedly the principal factor determining transfer enthalpies in this system, the cause of the exothermic $\delta\Delta H_s{}^r$ for *cis*-azobenzene must be the fact that solute-solvent interactions (*cis*-azobenzene-cyclohexanone) are greater than the solvent-solvent interactions of cyclohexanone (the "hole" energy). On the other hand the transition state appears to have lost some of these dipole-dipole interactions. Its solute-solvent (transition state-cyclohexanone) dipole-dipole interaction energy is apparently less than the cyclohexanone solvent-solvent interaction (the "hole" energy) and hence the transfer enthalpy, δH^t, is *endothermic*. What changes in geometry and electron distribution caused this loss in solute-cyclohexanone solvent interaction energy in the transition state?

The answer is not to be found in any possible resemblance between the transition state and the product. Although the product of this reaction, *trans*-azobenzene, has a zero dipole moment,[6] its solvent transfer enthalpy, $\delta\Delta H_s{}^P$, from cyclohexane to cyclohexanone is *exothermic* and only a little smaller than that of the reactant, *cis*-azobenzene (see Table III). This observation agrees with the findings of Fuchs[7,8] that in organic systems of this kind solvent transfer enthalpies are not too dependent on the overall molecular dipole moment. The solvent interacts with each functional group of the solute, each interaction making an additive contribution to the overall transfer enthalpy.[8]

The local interactions of interest in the solvation of *cis*- and *trans*-azobenzene are clearly those between the two N lone pair dipoles of the azobenzenes and the carbonyl group of cyclohexanone. When we consider the rotation mechanism transition state (Figure 3) we see that these two dipoles are maintained throughout the course of the rotation. The magnitude of the interaction between these two dipoles and solvent molecules should therefore be intermediate between that found in the reactant and that found in the product. This is not observed.

On the other hand, in the nitrogen inversion mechanism (Figure 3) one of the N lone pair dipoles disappears entirely

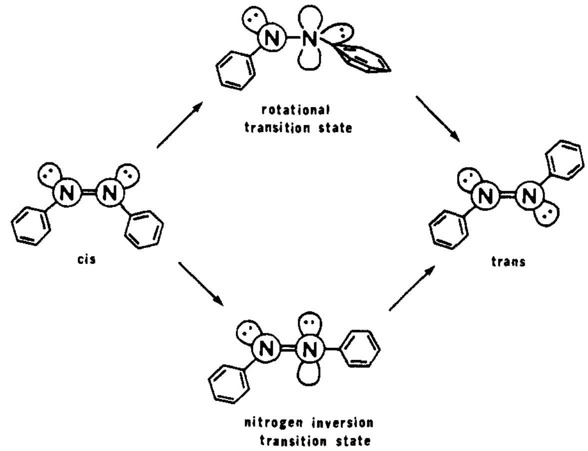

Figure 3.

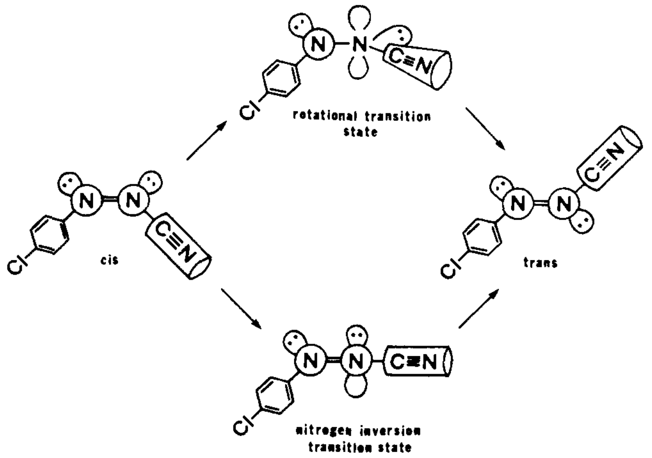

Figure 4.

(it is converted into a p orbital on the sp hybridized N). This would cause the substantial loss in the solute-cyclohexanone solvent interaction energy in the transition state, which is in fact observed.

The data and the arguments for the case of the *cis-p*-chlorobenzenediazocyanide are substantially the same. The enthalpies of solvent transfer (cyclohexane → cyclohexanone) for both the cis and the trans cyanide are larger than for the azobenzenes. This is clearly due to the fact that we have here, in addition to the two N lone pair dipoles, another two dipoles, namely the C≡N and the Ph—Cl dipoles. Since now three of these four dipoles are maintained throughout the nitrogen inversion process (Figure 4) the transition state enthalpy of transfer, δH^{t}, does not actually become endothermic, it is merely reduced to about zero (Figure 2). The rotational mechanism would again predict a δH^{t} value intermediate between the enthalpy of transfer of the reactants and the products ($\delta\Delta H_{\mathrm{s}}^{\mathrm{r}}$ and $\delta\Delta H_{\mathrm{s}}^{\mathrm{p}}$). This would be a substantial, exothermic transfer enthalpy, which is in fact not observed. The nitrogen inversion mechanism, on the other hand, would, as before, predict a reduction in the δH^{t} value below that of the $\delta\Delta H_{\mathrm{s}}^{\mathrm{r}}$ and $\delta\Delta H_{\mathrm{s}}^{\mathrm{p}}$ values. This is in fact observed and we therefore believe that the nitrogen inversion mechanism is operating here also.

It may well be that for certain unusual azo compounds, such as the para-donor/para′-acceptor substituted azobenzenes studied by Whitten and coworkers,[4] the rotational mechanism may provide the pathway of lower energy. In general, however, it is probably the availability of the nitrogen inversion mechanism which makes N═N bonds more geometrically labile than C═C bonds.

Experimental Section

Materials. Azobenzene (Eastman) dissolved in petroleum ether was irradiated (G.E. sunlamp) and then fractionated on an alumina column using petroleum ether and 10:1 petroleum ether-methanol as eluents. This yielded *trans*-azobenzene, mp 68-69° (lit.[1a] mp 68°), and *cis*-azobenzene, mp 69-70° (lit.[1a] mp 71°), mixture mp 44° (lit.[1a] eutectic 41°). *cis-p*-Chlorobenzenediazocyanide, mp 29-30° (lit.[2] mp 29°) was prepared by treatment of *p*-chlorobenzenediazonium chloride with HCN.[2] *trans-p*-Chlorobenzenediazocyanide, mp 104-105° (lit.[2] mp 105°), was obtained by allowing the cis compound to rearrange in cyclohexane solution at room temperature.

Heats of Solution. The calorimeter and the procedure employed have been described previously.[5]

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