

# Chemical Behavior of Charge-Transfer Complexes.

## III. Racemization of Optically Active Binaphthyl Donors in the Presence of Organic Acceptors<sup>1</sup>

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Rates of racemization of the aromatic donors (+)-9,10-dihydro-3,4;5,6-dibenzophenanthrene (I) and (+)-1,1'-binaphthyl (II) have been measured in pure solvents and in solutions containing acceptors. In nearly all instances, added acceptors produced rate enhancements. The largest effect observed was a 2.06-fold increase in the rate of racemization of I (dioxane, 33.68°) produced by 0.227 M trinitrofluorenone. For the racemization of (+)-I in *o*-dichlorobenzene at 108.1°, plots of observed rate constant vs. acceptor concentration, for the acceptors 1,3,5-trinitrobenzene and picryl chloride, are close to linear at lower acceptor concentrations and begin to level off at higher concentrations of acceptor. Catalytic effectiveness parallels acceptor strength for the two acceptors studied. These results are consistent with an explanation ascribing the rate enhancements entirely to charge-transfer complexing. For the racemization of (+)-II in *o*-dichlorobenzene at 33.7°, a plot of observed rate constant vs. concentration of 1,3,5-trinitrobenzene is linear over the entire concentration range studied. The same behavior is observed in dioxane solvent with the acceptors 1,3,5-trinitrobenzene, picryl chloride, and 2,4,7-trinitrofluorenone. Although catalytic effectiveness parallels acceptor strength for the first three acceptors, tetranitrofluorenone is no more effective than trinitrofluorenone. In dioxane, added trinitrofluorenone produces a decrease in both apparent enthalpy of activation and apparent entropy of activation. The rate enhancements in the racemization of 1,1'-binaphthyl can be ascribed entirely to charge-transfer complexing only if the equilibrium constant for 1:1 complex formation with trinitrobenzene in *o*-dichlorobenzene at 33.7° is approximately 0.5 l. mole<sup>-1</sup> or smaller.

### Introduction

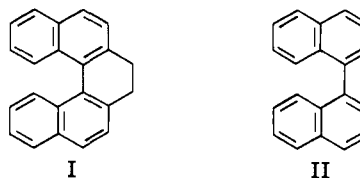
A reaction in which an organic donor passes through an activated state which is a stronger donor than the ground state might, under suitable conditions, be catalyzed by a nonreacting acceptor.<sup>1b</sup> An increase in donor strength could result from an increase in electron-richness or from an improvement in the geometrical requirements for complex formation, or both. Several independent studies have established that the complexing ability of both biphenyl donors<sup>3</sup> and

biphenyl acceptors<sup>4</sup> is greatly decreased when the two aromatic rings cannot be coplanar. Racemization of an optically active biphenyl is generally assumed to involve an approximately coplanar transition state<sup>5</sup>; consequently, we might expect the rate of racemization of a biphenyl donor to be increased by added acceptors.<sup>6</sup>

As part of a study of solvent effects in biphenyl racemizations, Graybill and Leffler<sup>6</sup> briefly examined the effect of aromatic acceptors on the rate of racemization of 2,2'-dimethoxy-6,6'-dicarbomethoxybiphenyl. In chloroform solvent at 100°, 0.23 M 1,3,5-trinitrobenzene produced a 14% increase in rate, while the effect of 0.07 M 2,4,7-trinitrofluorenone in acetonitrile at 100° was close to the experimental uncertainty. This particular biphenyl may not have been an ideal choice for a study of catalysis by charge-transfer complexing for two reasons. First, the electron-withdrawing carbomethoxy groups greatly reduce the donor strength.<sup>3a</sup> Secondly, there is a possibility of n- $\pi$  interaction between the oxygen atoms in the donor and the acceptor. Such interaction, by increasing the effective size of the barrier groups, could obscure any catalytic effects resulting from  $\pi$ - $\pi$  interaction.<sup>7</sup> For these reasons, a more detailed study of this question, avoiding possible complications due to polar barrier groups or other groups having unshared electrons, seemed in order.

### Results

The compounds investigated in this work were (+)-9,10-dihydro-3,4;5,6-dibenzophenanthrene (I) and (+)-1,1'-binaphthyl (II). Compound I was synthesized



(c) C. E. Castro, L. J. Andrews, and R. M. Keefer, *ibid.*, **80**, 2322 (1958); (d) for closely similar results involving 1-cyclopentenyl- and 1-cyclohexenyl-naphthalenes, see L. H. Klemm, J. W. Sprague, and H. Ziffer, *J. Org. Chem.*, **20**, 200 (1955).

(4) M. S. Newman, "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956, Chapter 10.

(5) F. H. Westheimer in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, Chapter 12.

(6) B. M. Graybill and J. E. Leffler, *J. Phys. Chem.*, **63**, 1461 (1959).

(7) At the time the present study was initiated, the significance of the results of Graybill and Leffler<sup>6</sup> seemed clouded by another consideration. Appreciable kinetic solvent effects were observed in these studies, the rates showing a general increase with increasing solvent polarity. The effect of trinitrobenzene in chloroform is therefore in the direction expected for a solvent effect not involving charge-transfer complexing. Although it seemed logical to attribute the solvent effects to the polar barrier groups, subsequent work has revealed solvent effects of similar magnitude in the racemization of 1,1'-binaphthyl (A. K. Colter and L. M. Clemens, *ibid.*, **68**, 651 (1964)).

(1) (a) Abstracted in part from a thesis submitted by L. M. C. in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the Carnegie Institute of Technology, June 1963; (b) part II of this series: A. K. Colter, S. S. Wang, G. H. Megerle, and P. S. Ossip, *J. Am. Chem. Soc.*, **86**, 3106 (1964).

(2) National Science Foundation Cooperative Fellow, 1961-1962.

(3) (a) C. B. Coleman, Abstracts, 128th National Meeting of the American Chemical Society, Minneapolis, Minn., Sept. 1955, p. 4-O; (b) C. E. Castro and L. J. Andrews, *J. Am. Chem. Soc.*, **77**, 5198 (1955);

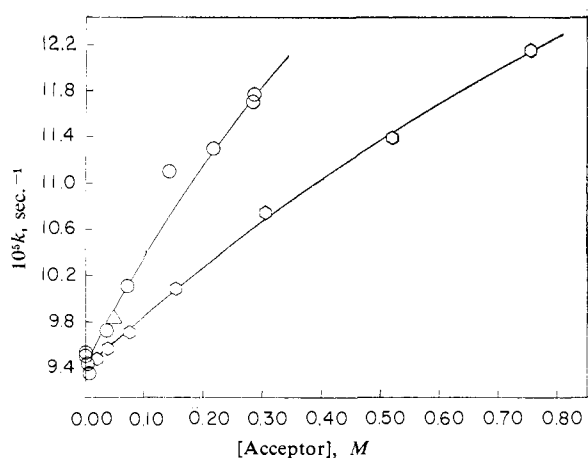


Figure 1. Racemization of 9,10-dihydro-3,4;5,6-dibenzophenanthrene in *o*-dichlorobenzene at 108.1° in the presence of aromatic acceptors: O, TNB; Δ, TNF; □, PC.

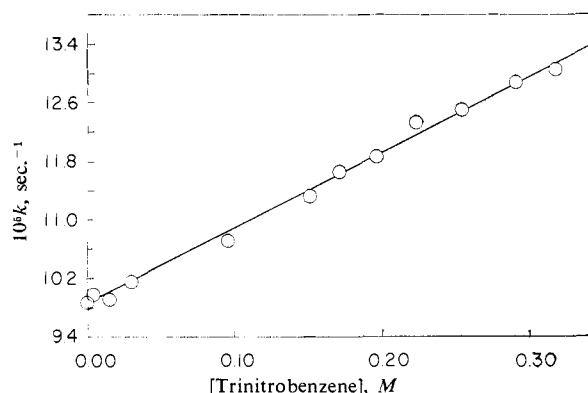


Figure 2. Racemization of 1,1'-binaphthyl in *o*-dichlorobenzene at 33.68° in the presence of 1,3,5-trinitrobenzene.

by the method of Hall and Turner.<sup>8</sup> The few modifications in procedure and differences in results are described in the Experimental section. Compound II was prepared by a method patterned after that outlined in a preliminary communication by Harris and Mellor<sup>9</sup> (see Experimental).

**Kinetic Studies.** The effect of acceptors on the rates of racemization of the binaphthyls is shown by the results in Tables I and II. Strict first-order behavior through three half-lives was observed in all cases. The variety and concentration ranges of acceptors which could be studied was severely limited by solubility and by the range and intensity of the charge-transfer absorption. Thus, although the solubility of tetracyanoethylene in *o*-dichlorobenzene is about 0.025 *M* at 25°, solutions 0.025 *M* in tetracyanoethylene and 0.029 *M* in 1,1'-binaphthyl are too intensely colored (broad maximum at 580–590 *mμ*) to permit visual polarimetry. The same difficulty prevented a study of higher concentrations of chloranil in dioxane; the single concentration of chloranil studied in *o*-dichlorobenzene (Table II) is close to saturation. Table III summarizes the results of a study of the effect of trinitrofluorenone on the activation parameters for racemization of 1,1'-binaphthyl in dioxane. The de-

(8) D. M. Hall and E. E. Turner, *J. Chem. Soc.*, 1242 (1955).

(9) M. M. Harris and A. S. Mellor, *Chem. Ind.* (London), 1082 (1961).

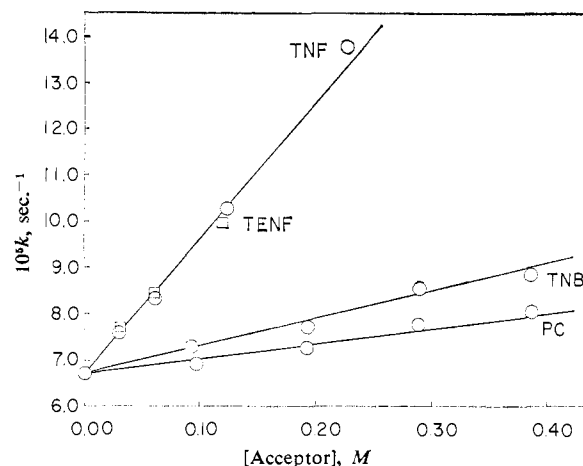


Figure 3. Racemization of 1,1'-binaphthyl in dioxane at 33.68° in the presence of aromatic acceptors.

pendence of the rates of racemization of I and II on acceptor concentration are shown graphically in Figures 1, 2, and 3.

Table I. Racemization of 9,10-Dihydro-3,4;5,6-dibenzophenanthrene<sup>a</sup> in *o*-Dichlorobenzene at 108.1°<sup>b</sup> in the Presence of Acceptors

Acceptor <sup>c</sup>	[Acceptor], <i>M</i> <sup>d</sup>	10 <sup>6</sup> <i>k</i> , sec. <sup>-1e</sup>	
None	...	9.51 ± 0.08	
	...	9.54 ± 0.23	
TNB	0.0041	9.44 ± 0.10	
	0.0070	9.35 ± 0.17	
	0.0359	9.73 ± 0.23	
	0.0714	10.11 ± 0.13	
	0.1421	11.10 ± 0.19	
	0.2160	11.30 ± 0.13	
	0.2833	11.63 ± 0.21 <sup>f</sup>	
	0.2843	11.71 ± 0.56 <sup>g</sup>	
	0.2850	11.77 ± 0.20 <sup>g</sup>	
	PC	0.0201	9.48 ± 0.07
		0.0381	9.57 ± 0.04
0.0755		9.71 ± 0.07	
0.1522		10.08 ± 0.05	
0.3047		10.75 ± 0.08	
0.5194		11.38 ± 0.14	
TNF	0.7536	12.15 ± 0.28	
	0.0484	9.83 ± 0.18	

<sup>a</sup> Concentration of donor = 7.0 × 10<sup>-3</sup> *M* unless otherwise noted. <sup>b</sup> Temperature maintained at 108.1 ± 0.1° unless otherwise noted. <sup>c</sup> TNB = 1,3,5-trinitrobenzene; PC = picryl chloride; TNF = 2,4,7-trinitrofluorenone. <sup>d</sup> All concentrations refer to 108.1°. <sup>e</sup> Rate constants listed with average deviations (see Experimental). <sup>f</sup> Temperature, 108.0 ± 0.1°. <sup>g</sup> Donor concentration = 3.5 × 10<sup>-3</sup> *M*.

**Relative Acceptor Strengths of the Polynitro Compounds.** In comparing the catalytic effectiveness of the polynitroaromatic acceptors, it is useful to have a measure of the relative acceptor strengths of these compounds. Briegleb<sup>10</sup> has shown that for complexes of a single acceptor with a homologous series of donors (e.g., benzene, toluene, xylene, etc.) a linear relation exists between the frequency of the long wave-length absorption band of the complex and the free energy of complex formation. A similar relationship has been

(10) G. Briegleb, "Elektronen-Donator-Acceptor-Komplexe," Springer-Verlag, Berlin, 1961, pp. 133–147.

**Table II.** Racemization of 1,1'-Binaphthyl<sup>a</sup> at 33.68 ± 0.03° in the Presence of Acceptors

Solvent	Acceptor <sup>b</sup>	[Acceptor], M <sup>c</sup>	10 <sup>5</sup> k, sec. <sup>-1d</sup>		
o-Dichlorobenzene	None	...	9.86		
		...	9.87		
		...	9.89 <sup>e</sup>		
	TNB	0.0037	9.98 <sup>e</sup>		
		0.0075	9.91		
		0.0301	10.15		
		0.0947	10.71		
		0.1510	11.33		
		0.1708	11.66		
		0.1962	11.86		
		0.1962	11.77 <sup>f</sup>		
		0.2226	12.33		
		0.2544	12.50		
		0.2907	12.88		
		0.3178	13.05		
		TCNE <sup>g</sup>	0.0028	9.87 <sup>e</sup>	
			CA <sup>h</sup>	0.0131	9.59 <sup>e</sup>
		Dioxane	None	...	6.68
				...	6.68
				...	6.91
PC	0.0966		6.91		
	0.1932		7.26		
	0.2890		7.75		
	0.3865		8.02		
	0.0930		7.27		
	0.1934		7.68		
	0.2900		8.53		
0.3867	8.81				
TNB	0.0311		7.58		
	0.0622		8.56		
	0.1244		10.26		
	0.2272		13.76		
	0.0301		7.65 <sup>e</sup>		
TNF	0.0601		8.43		
	0.1203		9.93		
	0.0485		6.84		
	TAPA <sup>i</sup>		0.1643	11.21 <sup>e</sup>	
	None	...	5.04 <sup>h</sup>		
TNB		0.1851	6.45 <sup>h</sup>		
SnCl <sub>4</sub>		0.187	5.16		

<sup>a</sup> Concentration of 1,1'-binaphthyl = 2.91 to 2.94 × 10<sup>-2</sup> M unless otherwise noted. <sup>b</sup> Abbreviations as in Table I. <sup>c</sup> All concentrations refer to 33.68°. <sup>d</sup> Estimated uncertainty ±1% or less unless otherwise noted (see Experimental). <sup>e</sup> Estimated uncertainty between 1 and 2%. <sup>f</sup> Concentration of 1,1'-binaphthyl = 3.91 × 10<sup>-2</sup> M. <sup>g</sup> Tetracyanoethylene. <sup>h</sup> Chloranil. <sup>i</sup> 2,4,5,7-Tetranitrofluorenone. <sup>j</sup> α-(2,4,5,7-Tetranitro-9-fluorenylideneaminoxy)propionic acid, [α]<sub>D</sub> -13°. <sup>k</sup> Concentration of 1,1'-binaphthyl = 5.87 × 10<sup>-2</sup> M.

demonstrated for the complexes of a homologous series of acceptors (specifically, a series of *p*-benzoquinones) with the single donor hexamethylbenzene.<sup>11</sup> Assuming that a similar relationship holds for complexes of picryl chloride (PC), 1,3,5-trinitrobenzene (TNB), 2,4,7-trinitrofluorenone (TNF), and 2,4,5,7-tetranitrofluorenone (TENF) with a single donor, then either of the two quantities, *K* (or Δ*G*<sup>0</sup>) for complex formation or λ<sub>max</sub> for the long wave-length charge-transfer absorption, could be used as at least a qualitative measure of acceptor strength. Ross, Bassin, and Kuntz<sup>12</sup> have established the order TNB > PC through equilibrium measurements; the equilibrium constants for 1:1 complex formation with anthracene in chloroform solution at 23.8° were found to be 3.6 and 1.26 l. mole<sup>-1</sup>, respectively, for the two acceptors. Measure-

(11) R. Foster, D. Ll. Hammick, and P. J. Placito, *J. Chem. Soc.*, 3881 (1956).

(12) S. D. Ross, M. Bassin, and J. Kuntz, *J. Am. Chem. Soc.*, 76 4176 (1954).

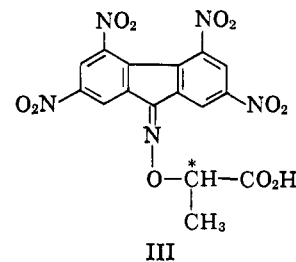
**Table III.** Temperature Dependence of the Rate of Racemization of 1,1'-Binaphthyl<sup>a</sup>

Temp., °C.	10 <sup>5</sup> k, sec. <sup>-1 b</sup>	Δ <i>H</i> <sup>*</sup> , kcal. mole <sup>-1</sup>	Δ <i>S</i> <sup>*</sup> , e.u. mole <sup>-1</sup>
Solvent, Dioxane			
33.68	6.68	21.61 ± 0.04 <sup>c</sup>	-7.27 ± 0.14 <sup>c</sup>
38.86	12.22		
43.91	21.66		
Solvent, Dioxane-0.2272 M Trinitrofluorenone			
33.68	13.76	20.37 ± 0.02 <sup>c</sup>	-9.88 ± 0.07 <sup>c</sup>
38.86	24.35		
43.91	41.76		

<sup>a</sup> Concentration = 0.029 M. <sup>b</sup> Estimated uncertainty, ±1%. <sup>c</sup> Uncertainties reflect scatter in log *k* vs. 1/*T* plot and not uncertainties in rate constants. Actual uncertainties are estimated to be not larger than ±0.2 kcal. mole<sup>-1</sup> in Δ*H*<sup>\*</sup> and ±0.6 e.u. mole<sup>-1</sup> in Δ*S*<sup>\*</sup>. <sup>d</sup> Concentration of TNF = 0.2272 M at the temperature of the rate measurement in all cases.

ments by Dewar and Lepley<sup>13</sup> of the charge-transfer maxima of complexes of TNB and TNF with polynuclear aromatic donors have established the order TNF > TNB. In the present work the positions of the charge-transfer maxima of the complexes of the four polynitroaromatic acceptors with the donor anthracene in chloroform solution were measured. The results were (in mμ): PC, 440 ± 5; TNB, 455 ± 5<sup>14</sup>; TNF, 540 ± 5<sup>15</sup> and 458 ± 5; TENF, 610 ± 10 and 510 ± 10. The order of acceptor strengths TENF > TNF > TNB > PC is thus established for aromatic donors.

**Mutarotation Studies.** In order to determine the effect of an asymmetric acceptor on the equilibrium (+)-1,1'-binaphthyl ⇌ (-)-1,1'-binaphthyl, a solution prepared from racemic 1,1'-binaphthyl and optically active α-(2,4,5,7-tetranitrofluorenylideneaminoxy)propionic acid (III)<sup>16</sup> was examined for mutarotation.



The study was complicated by some optical instability of III in dioxane solvent. Table IV summarizes the results of this study plus those of pertinent control experiments. Within experimental error, no mutarotation was observed. Mutarotation to a mixture containing a 1% excess of one enantiomer would result in a change in rotation of about 0.07°, which would be well beyond the limits of experimental uncertainty.

## Discussion

**Evidence for Catalysis by Charge-Transfer Complexing.** A reasonable mechanism for incursion of 1:1

(13) (a) M. J. S. Dewar and A. R. Lepley, *ibid.*, 83, 4560 (1961); (b) A. R. Lepley, *ibid.*, 84, 3577 (1962).

(14) A. Bier, *Rec. trav. chim.*, 75, 866 (1956), reports 460 mμ.

(15) A. P. Lepley, ref. 13b, reports 541 ± 4 mμ.

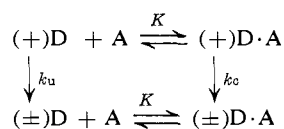
(16) M. S. Newman and W. B. Lutz, *J. Am. Chem. Soc.*, 78, 2468 (1956).

**Table IV.** Influence of Optically Active Acceptor on Racemic 1,1'-Binaphthyl in Dioxane at 33.9°

[TAPA], <sup>a</sup> M	Donor	[Donor], M	$\alpha_0$ , <sup>b,c</sup> deg.	$\alpha$ (after 24 hr.), <sup>c</sup> deg.	$\Delta\alpha$ , deg.
0.17	<i>dl</i> -1,1'-Bi- naphthyl	0.059	12.49	12.59	+0.10
0.17	Naphthalene	0.069	12.25	12.35	+0.10
0.17	None	...	12.53	12.63	+0.10

<sup>a</sup>  $\alpha$ -(2,4,5,7-Tetranitrofluorenylideneaminoxy)propionic acid,  $[\alpha]_D +86.7^\circ$ . <sup>b</sup> After allowing 15 min. for thermal equilibrium at 33.9°. <sup>c</sup> All rotations are averages of ten readings.

complexes in the racemization process is



In this scheme, A is the acceptor, D is the donor, and D·A is the 1:1 complex. The quantities  $k_u$  and  $k_c$  are the specific rates of racemization of uncomplexed and complexed biaryl, respectively;  $K$  is the equilibrium constant for 1:1 complex formation. Under conditions where the stoichiometric acceptor concentration  $[A]_0$  is much larger than the total concentration of 1:1 complexes, this mechanism leads directly to the following expression for the observed rate constant in the presence of added acceptor.<sup>1b</sup>

$$k_{\text{obsd}} = k_u + \frac{(k_c - k_u)K[A]_0}{1 + K[A]_0} \quad (1)$$

In theory, eq. 1 permits calculation of  $k_c$  and  $K$  from rate constants at two or more acceptor concentrations, provided  $k_u$ ,  $k_c$ , and  $K$  are constant over the range of acceptor concentrations studied. In the present work, however, the rate enhancements are far too small relative to the experimental uncertainties in the rate constants to permit such an analysis. Further, small but appreciable changes in  $k_u$ ,  $k_c$ , or  $K$  over the wide range of acceptor concentrations studied cannot be ruled out with any certainty.

Qualitatively, if the rate of racemization is influenced only by charge-transfer complexing, eq. 1 predicts a plot of  $k_{\text{obsd}}$  vs.  $[A]_0$  to have some downward curvature, the amount of curvature depending on the size of  $K$ . It is apparent then that the rate enhancements in the racemization of the bridged binaphthyl I (Figure 1) are in accord with the simple picture attributing all of the catalysis to 1:1 complexing.

In contrast, the plots of  $k_{\text{obsd}}$  vs.  $[A]_0$  for the racemization of 1,1'-binaphthyl (Figures 2 and 3) show no detectable curvature. Assuming that  $k_u$  and  $k_c$  do not change appreciably with acceptor concentration, it is possible to place an approximate upper limit on  $K$  for some of the systems studied. For the racemization of II in *o*-dichlorobenzene-TNB (Figure 2) and dioxane-TNF (Figure 3), for example,  $K$  cannot be greater than about 0.5 l. mole<sup>-1</sup> if  $k_u$  and  $k_c$  do not vary with  $[A]$ . If the simple picture is correct, the data indicate that the bridged binaphthyl I complexes to a much greater extent than 1,1'-binaphthyl. Equilibrium studies are planned in order to answer this question.

Perhaps the strongest evidence that a major portion of the rate enhancements are a result of charge-transfer complexing is the general correspondence between catalytic effectiveness and acceptor strength for the polynitroaromatic acceptors (Table V). The single

**Table V.** Catalytic Effectiveness of the Polynitroaromatic Acceptors

Acceptor <sup>a</sup>	Solvent	$10^6(k_c - k_u)K$ , l. mole <sup>-1</sup> sec. <sup>-1</sup> <sup>b</sup>
(+)-9,10-Dihydro-3,4,5,6-dibenzophenanthrene (I), 108.1°		
TNB	<i>o</i> -Dichlorobenzene	11
PC	<i>o</i> -Dichlorobenzene	4.6
(+)-1,1'-Binaphthyl (II), 33.68°		
TNB	<i>o</i> -Dichlorobenzene	10.2
TNB	Dioxane	5.9
PC	Dioxane	3.4
TNF	Dioxane	30
TENF	Dioxane	30

<sup>a</sup> Abbreviations as in Tables I and II. <sup>b</sup>  $10^6 \times$  initial slope of plot of  $k_{\text{obsd}}$  vs.  $[A]_0$ .

clear-cut exception is TENF, which is no more effective than TNF in catalyzing the racemization of 1,1'-binaphthyl in dioxane. The catalytic effectiveness depends on both  $k_c$  and  $K$ , but both of these quantities should increase with increasing acceptor strength.

Strong evidence for the charge-transfer complexing hypothesis is provided also by the size of the rate enhancements. Thus at 33.68°, 1,1'-binaphthyl racemizes more rapidly in dioxane-0.227 M TNF than in any of the 14 different one-component media in which racemization rates have been measured.<sup>9,17</sup> Thus, it seems clear that any nonspecific medium effect produced by 0.227 M TNF could not account for more than a fraction of the total rate enhancement.

Further evidence for the proposed mechanism of these rate enhancements is provided by the activation parameters summarized in Table III. The decrease in formal entropy of activation produced by added TNF is consistent with a mechanism in which a portion of the reaction involves complex formation.<sup>18</sup> Activation parameters for racemization of 1,1'-binaphthyl have been determined<sup>9,17</sup> in seven pure solvents, ranging in polarity from *n*-heptane to dimethylformamide. Entropies of activation (43.9°) in these solvents vary from -3.6 to -7.3 e.u. mole<sup>-1</sup>. The formal entropy of activation (43.9°) in dioxane-0.227 M TNF (-9.88 e.u. mole<sup>-1</sup>) is thus significantly lower than that observed in any pure solvent studied to date.

Several portions of the results which seemingly do not support the simple mechanism proposed must be given specific mention. First, one would predict the catalytic effectiveness of an acceptor to decrease in a donor solvent. Unexpectedly, the two rates in benzene solvent indicate that the catalytic effectiveness of TNB in this solvent ( $(k_c - k_u)K \approx 7.6$  l. moles<sup>-1</sup> sec.<sup>-1</sup>) is intermediate between that in dioxane and *o*-dichloro-

(17) A. K. Colter and L. M. Clemens, *J. Phys. Chem.*, **68**, 651 (1964).

(18) Similar changes were observed in the formal activation parameters for acetolysis of 2,4,7-trinitro-9-fluorenyl *p*-toluenesulfonate on addition of phenanthrene.<sup>1b</sup>

benzene. More rates in strong-donor solvents are needed to settle this question.

A second result not supporting the proposed mechanism is the absence of mutarotation of *dl*-1,1'-binaphthyl induced by (+)-TAPA (III). It may be argued, however, that the diastereomeric 1:1 complexes are of nearly equal stability so that the amount of mutarotation was too small to observe. Further, if the equilibrium constants for 1:1 complex formation between (+)-TAPA and the enantiomeric 1,1'-binaphthyls are both 0.5 l. mole<sup>-1</sup> or smaller, less than 8% of the total 1,1'-binaphthyl would be complexed under the conditions of the mutarotation experiment. It is interesting, in this respect, that Leffler and co-workers observed almost no mutarotation of *o*-(2-dimethylaminophenyl)phenyltrimethylammonium benzenesulfonate<sup>19</sup> and no mutarotation of 2,2'-dimethoxy-6,6'-dicarbomethoxybiphenyl<sup>16</sup> in *D*-2-methyl-1-butanol solvent.

Finally, the catalytic effects in the racemization of the bridged binaphthyl II are unexpectedly comparable in size to those in the racemization of I, even though the temperature of racemization of II (108.1°) is highly unfavorable for complex formation.

**Transition-State Characterization.** From eq. 1 it is easily confirmed that the initial slope of a plot of  $k_{\text{obsd}}/k_u$  vs.  $[A]_0 = ((k_c - k_u)/k_u)K$ . The "virtual equilibrium constant,"<sup>20</sup>  $K^*$ , for 1:1 complexing between acceptor and the transition state for the racemization =  $k_c K/k_u$ .<sup>1b</sup> In the present work, an estimate of  $K^*$  can be obtained as follows. The initial slope of a plot of  $k_{\text{obsd}}/k_u$  vs.  $[A]_0 = (k_c - k_u)K/k_u = K^* - K$ .<sup>21</sup> Thus, for the TNF-1,1'-binaphthyl system in dioxane at 33.68°, for example,  $K^* - K \approx (30/6.68) \times 10^5 = 4.5$  l. mole<sup>-1</sup>. If, then,  $K$  is less than about 0.5 l. mole<sup>-1</sup>,  $K^*$  lies in the range 4.5 to 5.0 l. mole<sup>-1</sup>. Together with sufficient equilibrium data for 1:1 complex formation or sufficiently complete correlations between  $K$  and  $\lambda_{\text{max}}$  for the long wave-length charge-transfer absorption<sup>10</sup> and between  $\lambda_{\text{max}}$  and calculated MO parameters,<sup>13</sup> such estimates of  $K^*$  could provide direct evidence for or against the assumed<sup>5</sup> coplanar transition state for racemization of hindered biaryls.

## Experimental

**Solvents and Acceptors.** Solvents were purified as previously described.<sup>17</sup> 1,3,5-Trinitrobenzene, Eastman Kodak reagent grade, was recrystallized once from ethanol and once from glacial acetic acid (m.p. 122.7–123.8°). This material was used in the racemizations of I. In the racemizations of II, Eastman Kodak indicator grade, m.p. 122.5–123.5°, was used without further purification. 2,4,7-Trinitrofluorenone was prepared by the method of Woolfolk and Orchin,<sup>22</sup> m.p. 176–177° (lit.<sup>22</sup> 175.2–176°). 2,4,5,7-Tetranitrofluorenone was prepared as described by Newman and Lutz,<sup>16</sup> m.p. 255–256° (lit.<sup>16</sup> 253.0–254.6°). (+)- $\alpha$ -(2,4,5,7-Tetranitro-9-fluorenylideneaminoxy)propionic acid (III) was prepared by the method of Newman and Lutz.<sup>16</sup> When twice crystallized from propionic

(19) J. E. Leffler and W. H. Graham, *J. Phys. Chem.*, **63**, 687 (1959).

(20) J. L. Kurz, *J. Am. Chem. Soc.*, **85**, 987 (1963).

(21) The statement that the initial slope of a plot of  $\log k_{\text{obsd}}$  vs. [catalyst] =  $k_c K/k_u$  (ref. 1b) is correct only if  $k_c \gg k_u$ .

(22) E. O. Woolfolk and M. Orchin, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 837.

acid-water mixtures, the compound had m.p. 148–152°,  $[\alpha]_D$  83.4° (dioxane) (lit.<sup>16</sup> m.p. 151–155° and  $[\alpha]_D$  +86.7°). When the product was dried at 100° (2.5 mm.) in the presence of P<sub>2</sub>O<sub>5</sub>, the melting range broadened to 140–150° and  $[\alpha]_D$  increased to +86.7°. For completely solvent-free material Newman and Lutz report m.p. ca. 280° dec. and  $[\alpha]_D$  +97.1. The compound used in the present work was probably slightly solvated and not as optically pure as the reported compound. The ultraviolet spectrum of the compound was unchanged by the drying procedure. Chloranil, Matheson Coleman and Bell, was sublimed once before using, m.p. (sealed tube) 291°. Tetracyanoethylene, Eastman Kodak, was sublimed twice to obtain white crystals, m.p. 199–201°. Stannic chloride, Baker, fuming anhydrous, reagent grade, was used without further purification. Anthracene, Eastman Kodak White Label, m.p. 216–218°, was used without further purification.

(+)-9,10-Dihydro-3,4;5,6-dibenzophenanthrene. The synthesis of this compound was patterned after the method of Hall and Turner.<sup>8</sup> Variations in procedure or data are described below.

(a) **Resolution of 1,1'-Binaphthyl-2,2'-dicarboxylic Acid.** Following the procedure of Hall and Turner, the less soluble quinine salt of the diacid was initially crystallized from ethanol-ether; the white salt thus obtained had m.p. 201–202° dec. and  $[\alpha]_D$  +269° (c 1.01, dioxane). Further crystallization from the same solvent increased the m.p. to 204.5–205.5° dec. and  $[\alpha]_D$  to +292°. Upon decomposition with sodium hydroxide, acidification, and drying at 120°, the (+) salt gave 1,1'-binaphthyl-2,2'-dicarboxylic acid, m.p. 270°,  $[\alpha]_D$  –110° (0.1 *N* NaOH).

Hall and Turner recrystallized the less soluble salt from pure ethanol and report m.p. 178° dec.,  $[\alpha]_{5791}$  –90° (acetone). Decomposition of this salt gave the (–) diacid, slightly hydrated, m.p. 120° dec.,  $[\alpha]_{5791}$  –109° (0.1 *N* NaOH). These authors note that the rotation of the less soluble salt in chloroform varied widely depending on the amount of ethanol present in the solvent as an impurity. In the present work the salt did not appear to be soluble in dry acetone.

The first workers to resolve the diacid, Kuhn and Albrecht,<sup>23</sup> recrystallized the less soluble quinine salt from ethanol-ether; the purest salt thus obtained had m.p. 197.5–198°,  $[\alpha]_D$  +302° (chloroform). Decomposition of this salt gave the (–) diacid, m.p. 274,  $[\alpha]_D$  –102° (0.1 *N* NaOH). The present results are therefore in closer agreement with those of Kuhn and Albrecht.

(b) (+)-9,10-Dihydro-3,4;5,6-dibenzophenanthrene. The optically active hydrocarbon was prepared from the reaction of (–)-2,2'-bisbromomethyl-1,1'-binaphthyl with phenyllithium, following the method of Hall and Turner. When the reaction mixture was evaporated to dryness and taken up in methyl ethyl ketone, the racemic hydrocarbon crystallized first, leaving the mother liquor enriched in optically active hydrocarbon and impurities. After most of the racemic hydrocarbon had crystallized, the mother liquor was evaporated to dryness and the resulting red glass chromatographed on silica gel eluting with cyclohexane.

(23) R. Kuhn and G. Albrecht, *Ann.*, **465**, 282 (1928).

This procedure afforded a clean separation of the active hydrocarbon from the impurities. Combination of the initial fractions gave the hydrocarbon as white plates, m.p. 213–215°,  $[\alpha]_D +1140^\circ$  (benzene) (lit.<sup>8</sup> m.p. 215–216°,  $[\alpha]_{5791} +1302$ ).

(+)-1,1'-Binaphthyl. The procedure was patterned after that outlined in a preliminary communication by Harris and Mellor<sup>9</sup> and differs from their detailed procedure<sup>24</sup> which was not available at the time of this work. The synthesis of optically active (+)-naphthidine  $\alpha$ -bromo- $\pi$ -camphorsulfonate was carried out as described by Theilacker and Hopp.<sup>25</sup> This salt was directly deaminated to (+)-1,1'-binaphthyl as follows. To a cold (0–5°) stirred solution containing 110 ml. of 30% hypophosphorous acid (Baker, purified), 90 ml. of water, and 2.3 ml. of concentrated HCl was added 3.45 g. of the (+)-naphthidine salt,  $[\alpha]_D +97^\circ$  (60% aqueous acetone), followed by 1.2 g. of sodium nitrite. After 2 hr. an additional 1.0 g. of sodium nitrite was added to the suspension. The stirring was continued for another 3 hr. at 0–5°. The flask was then lightly stoppered and stored in the refrigerator for 10 days during which time a total of 5 g. of sodium nitrite was added in small portions. The cold mixture was filtered and the filtrate washed several times with ice-cold 25% NaOH, ice-water, ice-cold 20% HCl, and finally with cold water again. After drying under vacuum, the pink residue was suspended in 250 ml. of 4% benzene-pentane and filtered; the filtrate was rapidly (suction) chromatographed on a silica gel column (14 g. of silica gel, 2.5-cm. o.d.) in a cold room (10–20°). After further elution with 500 ml. of 1% benzene-pentane, the first fraction, a colorless solution, was evaporated under vacuum in the cold to give the optically active binaphthyl, 0.35 g. (35%), as white crystals, m.p. 156–159°,  $[\alpha]_D +154^\circ$  (*c* 1.00, benzene). A second

fraction eluted with 250 ml. of 1% benzene-pentane gave 0.16 g. (17%), m.p. 157–160°,  $[\alpha]_D +192^\circ$ . Harris and Mellor<sup>9</sup> report m.p. 157–159°,  $[\alpha]_{5791} +245^\circ$ . Larger samples of binaphthyl were prepared in the same way by deamination of as much as 13 g. of the (+) salt. Yields (40–55%) and optical purity ( $[\alpha]_D +145$ – $165^\circ$ ) were fairly reproducible.

*Kinetic Measurements.* Rates of racemization of I were measured using a sealed ampoule technique. Eight ampoules (drawn from 3-in. Pyrex test tubes) were each filled with about 1.8 ml. of the kinetic solution and placed in a constant temperature bath maintained at  $108.1 \pm 0.1^\circ$ . Tubes were withdrawn from the bath at approximately 5, 14, 28, 42, 56, 70, and 84% reaction and quenched thermally. The infinity tube was removed after at least ten half-lives. The contents of the quenched ampoules were transferred to a 1-dm. polarimeter tube and rotations (averages of 12 readings) measured. Rotations were reproducible to  $\pm 0.01^\circ$ ; the initial reading was generally 2.30 to 2.40°. Rate constants were calculated using the equation

$$k = \frac{2.303}{t} \log \frac{\alpha_0 - \alpha_\infty}{\alpha_t - \alpha_\infty}$$

where  $\alpha_0$  and  $\alpha_\infty$  are initial and final rotations, respectively, and  $\alpha_t$  is the rotation at time *t*. Rate constants listed in Table I are averages of six values, listed with average deviations. The only product of the reaction, both in the absence of acceptor and in the presence of 0.3 *M* TNB, was shown to be racemic binaphthyl.

Rates of racemization of II were measured by following the decrease in rotation using a jacketed polarimeter tube maintained at constant temperature by circulation of water from a constant temperature bath. The method has been described.<sup>17</sup>

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(24) A. S. Cooke and M. M. Harris, *J. Chem. Soc.*, 2365 (1965).

(25) W. Theilacker and B. Hopp, *Ber.*, **92**, 2293 (1959).