[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA AT DAVIS]

Molecular Complexes of Hindered Biphenyl Derivatives

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The interactions of a series of methylbiphenyls with 1,3,5-trinitrobenzene to form 1:1 complexes in carbon tetrachloride have been studied spectrophotometrically. The complex stabilities increase as the biphenyl nucleus is increasingly methylated at *m*- and *p*-positions. *o*-Methylbiphenyls are poor donors; the equilibrium constants for the association of the nitro compound with bimesityl and with 2,2′,6,6′-tetramethylbiphenyl are very small. The enthalpy changes accompanying these interactions are uniformly low. Apparently a copolanar orientation of the biphenyl rings is required for maximum electronic interaction of donor and acceptor components. The acceptor strength of nitrobiphenyls is also to some degree dependent on orientational factors. The hexamethylbenzene complex of bipicryl in chloroform is much less stable than that of 1,3,5-trinitrobenzene. However, the complexes of these two acceptors with *p*-toluidine as a donor are of comparable stability. It is suggested that the amino group of this base is the center of donor activity.

Because of the unfavorable geometry of its components, an aromatic molecular complex of the donor–acceptor type may be much less stable than is predicted on the basis of electronic considerations. Hexaethylbenzene, for example, interacts only feebly with iodine, iodine monochloride[1,2] and chloranil,[3] since the six alkyl groups screen the π-electron cloud of the donor against penetration by the acceptor.

In a preliminary communication[4] a similar steric argument has been suggested to explain the fact that hindered biphenyl derivatives have a low capacity for coördination with 1,3,5-trinitrobenzene in carbon tetrachloride solution. The parallel ring plane arrangement of donor and acceptor molecules which is characteristic[5] of solid complexes of aromatic compounds with trinitrobenzene and related substances is apparently highly critical for maximum complex stability. It is possible that only one of the two aromatic nuclei of a biphenyl molecule is directly coördinated with the acceptor in a 1:1 complex. Nonetheless if the two biphenyl rings, because of restricted rotation about the central bond, cannot assume a coplanar conformation, neither ring may serve as a suitable coördination site. A complex configuration in which the nucleus of a trinitrobenzene acceptor lies parallel to one ring of a hindered biphenyl and close enough to establish charge-transfer interaction[6] seems highly improbable. Such an arrangement should result in unfavorable contacts between the free ring of the donor and the nitro groups which protrude from the acceptor ring.[7]

A detailed report of the work on complexes of hindered biphenyls is now presented. This includes a revision of the equilibrium constants reported previously[4] for 1,3,5-trinitrobenzene complexes of a series of polymethylbiphenyls and a tabulation of the heats of interaction. Experiments to test the acceptor properties of polynitrobiphenyls are described, and a brief discussion is given of the donor strength of hexaethylbenzene with respect to 1,3,5-trinitrobenzene as an acceptor.

Experimental

The Methylbiphenyls.—Biphenyl (Eastman Organic Chemicals) was recrystallized from 95% ethanol, m.p. 70–71°. *p*-Methylbiphenyl was prepared from *p*-toluidine and benzene.[8] The product which distilled from 140–160° (2 mm.) was crystallized repeatedly from methanol, m.p. 47–48°. *m*-Methylbiphenyl was synthesized from *m*-toluidine and benzene.[8] The product was fractionally distilled and a cut of b.p. 149–150° (20 mm.) and $n^{26.5}\mathrm{D}$ 1.5983 was collected (lit.[9] b.p. 148–150° (20 mm.)). *o*-Methylbiphenyl was prepared through aromatization[10] of *o*-tolylcyclohexene. A sample of b.p. 266–268° (760 mm.) and $n^{26.5}\mathrm{D}$ 1.3602 was obtained. On oxidation with neutral permanganate a sample of this material gave *o*-phenylbenzoic acid, m.p. 108–110°. *p,p*′-Bitolyl, m.p. 122°, was alternately prepared[11,12] by the reaction of *p*-tolylmagnesium iodide with cupric chloride or of *p*-tolylmagnesium bromide with cobaltous chloride in the presence of bromobenzene. *m,m*′-Bitolyl was prepared by these same[11,12] procedures from *m*-tolylmagnesium bromide. A water-white oil was obtained by fractionation of the product (b.p. 171.5–173° (42 mm.), $n^{27}\mathrm{D}$ 1.5981, m.p. 5°).

o,o′-Bitolyl was conveniently synthesized by treating the chilled Grignard reagent prepared from 100 g. (0.585 mole) of *o*-bromotoluene in 100 ml. of ether with 77.4 g. (0.59 mole) of anhydrous cobaltous chloride. A vigorous reaction occurred, and the mixture turned black. After the reaction subsided, the mixture was stirred under reflux for three hours. It was then poured onto a mixture of 500 g. of ice and 50 ml. of concentrated hydrochloric acid. The organic phase was neutralized, dried over magnesium sulfate and concentrated *in vacuo*. The crude product distilled over a range of 86–120° (0.5 mm.). This was fractionated to yield 8.8 g. of water-white oil (b.p. 256–259°, $n^{26.5}\mathrm{D}$ 1.5718, m.p. 16–17° (lit.[13] b.p. 256–259°, m.p. 17–18°).

To synthesize 2-phenylmesitylene[14] a suspension of 2.3 g.

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[1] (a) L. J. Andrews and R. M. Keefer, THIS JOURNAL, **74**, 4500 (1952); (b) M. Tamres, D. Virzi and S. Searles, *ibid.*, **75**, 4358 (1953).

[2] N. Ogimachi, L. J. Andrews and R. M. Keefer, *ibid.*, **77**, 4202 (1955).

[3] R. Foster, D. Ll. Hammick and B. N. Parsons, *J. Chem. Soc.*, 555 (1956).

[4] C. E. Castro and L. J. Andrews, THIS JOURNAL, **77**, 5189 (1955).

[5] (a) H. M. Powell and G. Huse, *J. Chem. Soc.*, 435 (1943); (b) J. S. Anderson, *Nature*, **140**, 583 (1937).

[6] R. S. Mulliken, THIS JOURNAL, **74**, 811 (1952); *J. Phys. Chem.*, **56**, 801 (1952).

[7] These arguments may equally well be applied in explaining the results of studies of 2,4,7-trinitrofluorenone complexes; *cf.* C. B. Coleman, Abstracts of Papers Presented at Minneapolis, Minn., Division of Organic Chemistry, American Chemical Society, Sept., 1955; L. H. Klemm, J. W. Sprague and H. Ziffer, *J. Org. Chem.*, **20**, 200 (1955).

[8] M. Gomberg and J. C. Pernert, THIS JOURNAL, **48**, 1372 (1926).

[9] I. R. Sherwood, W. F. Short and R. J. Stansfield, *J. Chem. Soc.* 1832 (1932).

[10] R. T. Arnold, C. Collins and W. Zenk, THIS JOURNAL, **62**, 984 (1940).

[11] E. E. Turner, *Proc. Roy. Soc. N. S. Wales*, **54**, 37 (1920).

[12] M. S. Kharasch and E. K. Fields, THIS JOURNAL, **63**, 2316 (1941).

[13] G. Egloff, "Physical Constants of Hydrocarbons," Vol. III, Reinhold Publishing Corp., New York, N. Y., 1946, p. 317.

[14] This synthesis was patterned after the procedure of Kharasch and Fields[12] for the preparation of a symmetrical biphenyl (Ar_2) through coupling of ArMgBr in the presence of bromobenzene and catalytic amounts of cobaltous chloride. Biphenyl and polyphenyls are also produced. In the present case 2-phenylmesitylene, along with a small amount of biphenyl, was formed in poor yield. This is

(0.018 mole) of anhydrous cobaltous chloride in 157 g. (1.0 mole) of bromobenzene was added in four portions to a chilled and stirred Grignard reagent prepared from 50 g. (0.25 mole) of 2-bromomesitylene in 50 ml. of anhydrous ether. The mixture was refluxed for four hours and allowed to stand overnight. It was then stirred with iced hydrochloric acid. The ether phase was neutralized, dried with magnesium sulfate and concentrated *in vacuo*. Fractionation of the residue on a spinning band column gave 1.7 g. of biphenyl (b.p. 115° (4 mm.) and m.p. 70°) and 9 g. of 2-phenylmesitylene (b.p. 124.3–124.9° (6 mm.) and $n^{25}\text{D}$ 1.5688).

Anal. Calcd. for $C_{15}H_{16}$: C, 91.78; H, 8.22. Found: C, 91.73; H, 8.31.

A sample of the product (0.5 ml.) was stirred for six minutes at −3° with 5 ml. each of concentrated nitric and sulfuric acids. The mixture was poured on ice. The precipitate which formed was collected and recrystallized from acetone to yield white prisms of 2,4,6-trimethyl-3,4′,5-trinitrobiphenyl, m.p. 216–217° (lit.[15] m.p. 216–217°).

As starting material in the synthesis of 2,2′,6,6′-tetramethylbiphenyl, 2,6-dimethylbromobenzene (b.p. 77° (9 mm.)) was prepared from 2,6-dimethylaniline by a procedure[16] similar to that described for the preparation of *o*-tolyl bromide. A suspension of 30.6 g. (0.225 mole) of cobaltous chloride in 100 ml. of ether was added slowly to the chilled and stirred Grignard reagent prepared from 39 g. (0.216 mole) of the bromo compound in 100 ml. of ether. After the addition was complete, the mixture was refluxed for two hours. The details of recovery of the crude product were similar to those described for the preceding synthesis. That fraction of the product which distilled from 113–120° (4.5 mm.) crystallized upon scratching. This material was recrystallized from ethanol to yield 7.2 g. of the tetramethylbiphenyl, m.p. 66.7–66.9° (lit.[17] m.p. 66–67°).

3,3′,5,5′-Tetramethylbiphenyl has not previously been described. It was prepared from the Grignard reagent of 3,5-dimethylbromobenzene (35.6 g., 0.20 mole) and 26 g. of anhydrous cobaltous chloride (0.22 mole) by essentially the same procedure as is described in the preceding paragraph. The starting bromide was prepared by deamination of 2,4-dimethyl-6-bromoaniline[18] by the procedure used[19] in obtaining the corresponding diethylbromobenzene. A fraction of the product which distilled from 125–135° (0.4 mm.) crystallized upon scratching. The 6.3 g. of material thus obtained was recrystallized from ethanol containing a trace of ether. The melting point of the tetramethylbiphenyl sample was 48.6–49°.

Anal. Calcd. for $C_{16}H_{18}$: C, 91.37; H, 8.63. Found: C, 91.20; H, 8.75.

One gram of the product was heated and refluxed for 50 hours with 6 g. of potassium permanganate in 200 ml. of water. The manganese dioxide precipitate was filtered. On addition of hydrochloric acid to the filtrate a precipitate of 0.41 g. of organic acid was obtained. This was refluxed for 24 hours in 130 ml. of 0.5 *N* methanolic hydrogen chloride. Crystals of 3,3′,5,5′-tetracarbomethoxybiphenyl were obtained on concentration of this solution. They were recrystallized from benzene to yield 0.3 g. of material of m.p. 209° (lit.[20] m.p. 209°).

Bimesityl, m.p. 100.5–101°, was prepared[21] by the directions of Moyer and Adams.

Other Reagents.—Bipicryl, m.p. 241–243°, was prepared from picryl chloride and copper powder[22] and was recrystallized repeatedly from acetic acid.

Eastman Organic Chemicals mesitylene, hexamethylbenzene, hexaethylbenzene, *p*-toluidine, *m*-dinitrobenzene and 1,3,5-trinitrobenzene were used. Sulfonation[23] procedures were employed in purifying the mesitylene, and the solids were recrystallized before use.

1,2,3-Trinitrobenzene, m.p. 128.5–129.5°, was synthesized from 2,6-dinitroaniline.[24]

Eastman Organic Chemicals Spectro Grade carbon tetrachloride and chloroform were used without further treatment.

The Equilibrium Studies.—To study each complex a series of five solutions was prepared in which the donor concentrations were varied by a factor of approximately ten (usually 0.05–0.4 *M*); the acceptor concentrations were of the order of 10^{-2}–10^{-4} *M*. The optical densities of these solutions were measured in the Beckman spectrophotometer against solutions of corresponding concentration of the donor at various wave lengths in the 320–400 mμ region. The concentrations were chosen in most cases to provide optical density readings between 0.3 and 0.7. Details of temperature control are given elsewhere.[25]

The molar extinction coefficients of 1,3,5-trinitrobenzene in carbon tetrachloride were found to be identical with those of this acceptor in chloroform[26] in the 300–400 mμ region. Below 365 mμ the values were found to increase slightly with temperature. The extinction coefficients for other acceptors which are later reported as required in the discussion, were not sensitive to the temperature at which they were measured.

Equilibrium constants K_C for the formation of 1:1 complexes were obtained from the spectrophotometric data using equation 1 as described previously.[2]

$$1/(\epsilon_a - \epsilon_A) = 1/K_C(D)(\epsilon_c - \epsilon_A) + 1/(\epsilon_c - \epsilon_A) \quad (1)$$

In this equation ϵ_A and ϵ_c are, respectively, the extinction coefficients of the acceptor and of the complex. The donor concentration is represented by (D) and $\epsilon_a = d/(A)_t l$ where d is the measured optical density of the solution, l is the cell width and $(A)_t$ is the total (free and complexed) acceptor concentration.

The K_C values which are reported later are based on the use of mole/liter units for all substances in equilibrium. Values of K_N, a constant which relates the concentration of the donor in mole fraction units to those of the acceptor and the complex in mole/liter units, may be calculated from K_C values and the molar volumes of the solvent and the donor as discussed earlier.[2] The molar volumes of the various donors in carbon tetrachloride were determined by measuring the total volume of mixtures of the solvent and solute of known composition. The molar volumes (in liters) found at 25° are: biphenyl, 0.15; *o*-, *m*- and *p*-methylbiphenyl, 0.17; 2-phenylmesitylene, 0.20; *p,p*′-bitolyl, 0.19; *o,o*′- and *m,m*′-bitolyl, 0.18; 3,3′,5,5′- and 2,2′,6,6′-tetramethylbiphenyl, 0.22; and bimesityl, 0.26. In chloroform at 25° the molar volumes are: hexamethylbenzene, 0.18; and *p*-toluidine, 0.11. The values for carbon tetrachloride and chloroform at 25° are, respectively, 0.097 and 0.081.

The values of $\Delta H^0{}_C$ were calculated from the ratios of slopes of plots of the data according to equation 1 at the temperatures in question. In using this method of evaluation it was assumed that $\epsilon_c - \epsilon_A$ did not change with temperature (note the temperature independence of intercepts in Fig. 1). To obtain $\Delta H^0{}_N$ (donor concentration in mole fraction units) 0.2 kcal./mole should be subtracted from $\Delta H^0{}_C$ (donor concentration in mole per liter units).[27]

Solid Complexes.—The complexes described below were isolated in solid form to establish the 1:1 component ratio.

(a) ***p,p*′-Bitolyl and 1,3,5-Trinitrobenzene.**—Equal amounts (100 mg.) of the components were melted in a test-tube by gentle heating. The yellow solid which formed on cooling was dissolved in hot ethanol. Bright yellow rods of the 1:1 complex separated on cooling, m.p. 93.5–98.5°.

Anal. Calcd. for 1:1 complex: N, 10.63. Found: N, 10.17.

(b) **Hexamethylbenzene and 1,3,5-Trinitrobenzene.**—Solutions of 200 mg. of each component in a minimum volume of hot carbon tetrachloride were mixed. On cooling rectangular plates, m.p. 148–150°, of the 1:1 complex separated.

Anal. Calcd. for 1:1 complex: N, 11.19. Found: N, 11.09.

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apparently the first case in which a symmetrical biaryl has been obtained as a product of this type of reaction. To account for its formation some modification of the reaction mechanism proposed by Kharasch and Fields is required.

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(21) W. W. Moyer and R. Adams, THIS JOURNAL, **51**, 632 (1929).

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(25) R. M. Keefer and L. J. Andrews, THIS JOURNAL, **77**, 2164 (1955).

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Results

Hindered Biphenyl Donors.—Solutions of 1,3,5-trinitrobenzene and the various methylbiphenyls in carbon tetrachloride show strong absorption in the near ultraviolet region, which is presumed to be characteristic of 1:1 complexes. Typical values of K_C and ϵ_c for the biphenyl complex, which were calculated (equation 1) from spectrophotometric data taken in the 315–380 mμ region, are listed in Table I. Typical plots of data required for the evaluation of the equilibrium constants, the extinction coefficients and the heats of formation of the *p,p'*-bitolyl and bimesityl complexes at several temperatures are shown in Fig. 1.

Table I

The Biphenyl–1,3,5-trinitrobenzene Complex (CCl_4, 25°)

λ, mμ	K_C, l./mole	ϵ_{TNB}	ϵ_c
315	0.90	282	2200
360	.92	150	1360
370	.96	105	910
380	1.02	67	490

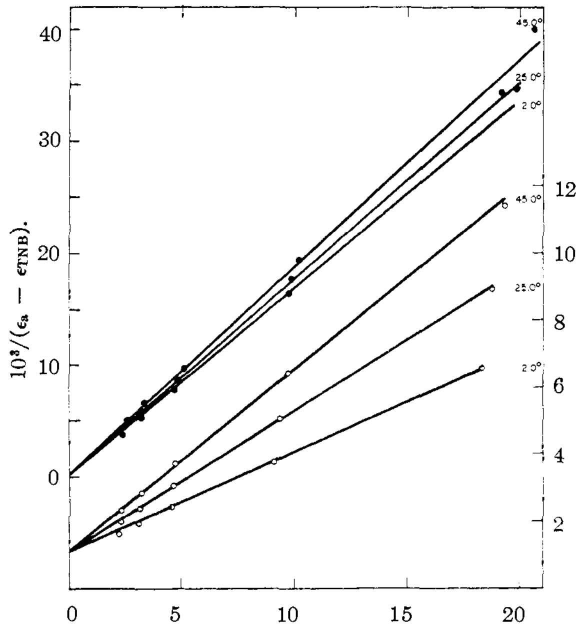

Fig. 1.—The effects of temperature on K_C and ϵ_C values (see equation 1) for 1,3,5-trinitrobenzene complexes in carbon tetrachloride. The open circles and the right-hand ordinate scale apply to *p,p'*-bitolyl as a donor. The filled circles and left-hand ordinate apply to bimesityl as a donor. The bitolyl complex was measured at 385 mμ and the bismesityl complex at 345 mμ.

Table II is presented to summarize the equilibrium constants and heats of complex formation for all of the methylbiphenyls. The K_C values which are reported are averages resulting from duplicate sets of measurements and are in several cases based on data taken at more than one wave length.[28]

The heats of formation were calculated from the slopes of plots of data taken at a single wave length in the region of strong complex absorption (see Fig. 1). The ΔH^0_C values are calculated from slopes based on measurements at 2 and 25° and at 25 and 45°. In general a single set of solutions was employed in obtaining the data required for these calculations.

Table II

Summary of Equilibrium Constants, Heats of Formation and Extinction Coefficients of the Complexes of 1,3,5-Trinitrobenzene with the Methylbiphenyls (CCl_4)

Donor	K_C (25.0°), l./mole	$-\Delta H_C{}^0$, kcal./mole 2, 25°	25, 45°	λ_{max},[a] mμ	$10^3\ \epsilon_c$
Biphenyl	1.0	2.38	2.33	<305	2.4[b]
p-Methylbiphenyl	1.6	1.96	1.72	360	1.1
m-Methylbiphenyl	1.2	1.03	1.17	350[c]	1.3
o-Methylbiphenyl	0.7	Av. 1.2		310	2.0
p,p'-Bitolyl[d]	2.3	2.82	2.14	380	1.1
m,m'-Bitolyl	2.0	2.34	1.98	365[c]	1.1
o,o'-Bitolyl	0.4	1.98	1.74	315	2.7
3,3',5,5'-Tetramethylbiphenyl	3.7	3.21	2.82	330	1.9
2,2',6,6'-Tetramethylbiphenyl	<0.1	<0.2	<0.2	320	?
Bimesityl	<0.1	0.4	0.3	340	?
2-Phenylmesitylene	0.45	1.80	0.96	330–340	2.4
Mesitylene	1.0	2.31	2.13	330	2.5

[a] The extinction coefficient of trinitrobenzene in carbon tetrachloride increases from 20 to 400 as the wave length is reduced from 400 to 300 mμ. [b] At 305 mμ. [c] An inflection point. The extinction coefficient increases as the wave length is lowered. [d] A solid 1:1 *p,p'*-bitolyl complex was prepared and identified (see Experimental section).

As can be anticipated[1,2] the complexes of these donors increase in stability as the number of *m*- and *p*-methyl substituents on the biphenyl nucleus is increased. The introduction of even a single *o*-methyl group has a destabilizing effect; this becomes extreme when all *o*-positions are substituted. The donor strengths of 2,2',6,6'-tetramethylbiphenyl and bimesityl are very low. The intercepts obtained in the graphical analysis of the spectrophotometric data for these compounds (see Fig. 1 for bimesityl) are very close to zero and can be used only to establish upper limits for the equilibrium constants. In these cases the observed absorption may result entirely from contact charge-transfer[29] rather than from photoactivation of a true complex. The observed change in equilibrium constants with changes in donor in the series mesitylene ~ biphenyl > 2-phenymesitylene >> bimesityl is indicative of the dependence of complex stability on the factors which prevent coplanarity of the two biphenyl rings.

The interactions to form complexes are, in general, very mildly exothermic. The ΔH^0_C values

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(28) The equilibrium constants expressed in reciprocal mole fraction units, K_N, are approximately ten times as large as the corresponding K_C values; the choice of units is immaterial as far as the present discussion is concerned. Molar volumes of the donors and the solvent, which are required for the calculation of K_N from K_C, are listed in the Experimental section for the use of interested readers.

(29) L. E. Orgel and R. S. Mulliken, This Journal, **79**, 4839 (1957).

for reactions of donors which bear four *o*-methyl substituents are very small in magnitude. It is certain, therefore, that when these highly hindered donors coördinate with 1,3,5-trinitrobenzene, the two biphenyl rings must retain a non-coplanar orientation. Rather the donor and acceptor molecules must be so oriented with respect to each other that only the feeblest forces of interaction can be established, if indeed they are established at all. If as a complex formed the two donor rings were forced into the same plane, the reactions of bimesityl and of 2,2′,6,6′-tetramethylbiphenyl would be highly endothermic, and the $\Delta H^0{}_C$ values would approach the energy of activation for racemization of a highly hindered optically active biphenyl.[30]

The values of ΔS^0 at 25° for the interactions, described in Table II averaged −6 e.u. No correlation of the changes in ΔH^0 with those in ΔS^0 or ΔF^0, such as has been made for polyalkylbenzene–halogen complexes, can be made in this case; actually the small ΔH^0 values are not accurately enough known so that ΔS^0 values can be estimated reliably.

The complex absorption maxima in the 300–400 mμ range, when they were located, were found to be rather broad (10–30 mμ). It seems probable that the major absorption band of the complexes, at least in some instances, occurs at lower wave lengths than those in which measurements were made. The spectra of the complexes of *m*-methylbiphenyl and *m,m′*-bitolyl are illustrative. The intensity of absorption in these cases increases as the wave length is reduced to about 360 mμ. It then remains relatively constant over a 10-mμ interval without reaching a pronounced maximum and finally increases continuously as the wave length is further reduced to 320 mμ. The spectra of the complexes below 300 mμ could not be determined because of the intense absorption of the solvent and the donors at low wave lengths. Since the λ_{max} and ϵ_c values reported in Table II do not reliably define the region and intensity of major charge-transfer absorption, their theoretical significance (as regards the Mulliken theory of complex formation[6,29]) is very limited.

Within the limits of error of the measurements it was found that the extinction coefficients of the complexes were temperature independent over the 2–45° range. This is clearly illustrated in Fig. 1 in which the intercept ($1/\epsilon_c$-ϵ_{TNB}) of the plots of data for the *p,p′*-bitolyl complex is shown to be unaffected by temperature changes. With the reservation that the rather small variation in temperature does not serve to test rigorously the constancy of ϵ_c values, it can be stated that only a single kind of 1:1 complex is formed in each of the interactions which has been studied.[29]

Bipicryl as an Acceptor.—Polynitroaromatic compounds generally function effectively as acceptors in forming complexes with aromatic hydrocarbons and amines. Highly hindered polynitrobiphenyls, however, should prove to be poor complexing agents for the same reason that has been advanced to explain the low donor strength of the *o*-methylbiphenyls.[31] To test this point it was planned originally to compare the acceptor properties of several polynitrobiphenyls including the 2,2′,4,4′,6,6′- and 3,3′,4,4′,5,5′-hexanitro compounds with those of the 1,3,5- and 1,2,3-trinitrobenzenes. Unfortunately the latter hexanitro derivative and several potentially useful tetranitro derivatives could not be prepared. Rather interesting results were obtained, however, from spectrophotometric studies of the stabilities of complexes of 2,2′,4,4′,6,6′-hexanitrobiphenyl (bipicryl). The methods used were very similar to those discussed in preceding paragraphs.

Both *p*-toluidine and hexamethylbenzene were employed as donors, and equilibrium constants and $\Delta H^0{}_C$ values for their interaction with bipicryl and with 1,3,5-trinitrobenzene were determined using chloroform as the solvent. The results, along with those of incidental studies of the hexaethylbenzene–1,3,5-trinitrobenzene and hexamethylbenzene–1,2,3-trinitrobenzene interactions in chloroform, are reported in Table III. Chloroform, rather than carbon tetrachloride, was used since bipicryl has an extremely low solubility in the tetrahalide. It is regrettable that the complexes of nitro compounds are much less stable in chloroform than in carbon tetrachloride.[32]

TABLE III

COMPLEXES WITH VARIOUS NITROAROMATICS IN CHLOROFORM

Donor	K_C (25.0°), l./mole	$-\Delta H^0{}_C$, kcal./mole 2, 25°	$-\Delta H^0{}_C$, kcal./mole 25, 45°	λ_{max}, mμ	10^3 ϵ_c
1,3,5-Trinitrobenzene complexes					
p-Toluidine[a]	0.56	1.40	1.42	430	1.5
Hexamethylbenzene[b]	0.80	1.56	1.70	390	2.4
Hexaethylbenzene	Very small	*ca.* 0		?	..
Bipicryl[c] complexes					
p-Toluidine	0.39	1.62	1.46	450	2.7
Hexamethylbenzene	<0.1	0	..	390	?
1,2,3-Trinitrobenzene[d] complexes					
Hexamethylbenzene	1	0.2	0.6	<350	[e]

[a] The values of K_C and $\Delta H_C{}^0$ for this complex are in accord with the constants reported in ref. 32b. [b] A solid hexamethylbenzene–1,3,5-trinitrobenzene complex was prepared and identified (see Experimental section). [c] At 450 and 390 mμ, respectively, the ε values for bipicryl in chloroform are 1.6 and 194. [d] At 350 mμ the extinction coefficient of 1,2,3-trinitrobenzene in chloroform is 352. [e] At 350 mμ $\epsilon_c = 9 \times 10^2$.

The K_C values for interaction of hexamethylbenzene with both 1,2,3- and 1,3,5-trinitrobenzene are appreciable in magnitude; that for interaction with bipicryl is very small. With *p*-toluidine as the donor the bipicryl and 1,3,5-trinitrobenzene complexes are of comparable stability. Apparently the coplanar arrangement of the acceptor rings is

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[30] R. L. Shriner, R. Adams and C. S. Marvel, "Organic Chemistry," Vol. I, edited by H. Gilman, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 357.

[31] The fact that neither 2,2′,4,4′,6-pentanitro-3-methylbiphenyl nor 2,2′,4,4′,6-pentanitro-3-carboxybiphenyl readily form crystalline complexes with anthrancene has been explained in terms of a steric effect; M. S. Newman, "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956, p. 473.

[32] (a) G. Briegleb and J. Czekalla, *Z. Elektrochem.*, **59**, 184 (1955); (b) A. Bier, *Rec. trav. chim.*, **75**, 866 (1956).

not nearly so critical for formation of the amine complex as for that of the aromatic hydrocarbon. It is conceivable that the amino group of *p*-toluidine rather than the entire π-electron cloud of the aromatic nucleus may serve effectively as a center of donor activity. A much less intimate arrangement of the complex components may, therefore, be required than when hexamethylbenzene is the donor.

It has been suggested[26,33] that 2:1 and 1:2, as well as 1:1 complexes, may form to some extent in solutions of aromatic amines and polynitrobenzenes.[34] Although this matter was not thoroughly investigated in the present series of measurements on the *p*-toluidine complexes, there was no positive evidence for the formation of other than 1:1 type aggregates. In the spectrophotometric studies of both the bipicryl and 1,3,5-trinitrobenzene complexes the *p*-toluidine concentrations were varied from 0.1–0.8 M (the acceptor concentrations were of the order of 10^{-3} M). When the resultant data were interpreted graphically according to equation 1, very satisfactory linear plots were obtained.

It is interesting to observe that the low donor strength of hexaethylbenzene as compared to that of hexamethylbenzene is again manifested when 1,3,5-trinitrobenzene is the donor. The spectrum of the nitro compound in chloroform is so little enhanced by hexaethylbenzene that it is questionable whether *any* significant donor–acceptor interactions occur in solutions of the two substances.

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[33] S. D. Ross and M. Labes, This Journal, **79**, 76 (1957).

[34] See, however, R. Foster and D. Ll. Hammick, *J. Chem. Soc.*, 2685 (1954).

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Kinetic Isotope Effects in the Acetolyses of Deuterated Cyclopentyl Tosylates[1,2]

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The acetolysis rates of the tosylates of cyclopentanol, cyclopentanol-1-*d*,*cis*- and *trans*-cyclopentanol-2-*d* and cyclopentanol-2,2,5,5-d_4 are described. All of the deuterated compounds solvolyze significantly more slowly than does cyclopentyl tosylate itself. An analysis of the α-deuterium case based on statistical mechanics indicates that the isotope effect is due predominantly to the change of a tetrahedral C–H bending vibration to an "out-of-plane" deformation in the transition state. The β-deuterium isotope effect is ascribed to the change of a tetrahedral C–H bending mode to a vibration in the transition state along a molecular orbital resulting from increased hyperconjugation in the electron deficient system. An argument is advanced for discounting any important specific solvation of the β-hydrogens in the solvolyzing molecule.

The isotope effect in solvolytic reactions derived from the substitution of β-hydrogens by deuterium in a substrate molecule was first exploited by Shiner[3] and by Lewis[4] and was demonstrated by them to be a valuable new tool in understanding such reactions.[5] In the present work, we wished to determine the isotope effect derived from an α-deuterium atom and the effect of stereochemical configuration of a β-deuterium, independent of conformational differences. For these purposes, we prepared the tosylates of cyclopentanol-1-*d* (I), *cis*- and *trans*-cyclopentanol-2-*d* (*cis*-II and *trans*-II, respectively) and of cyclopentanol-2,2,5,5-d_4 (III) and determined the solvolysis rates in acetic acid.

Preparation of Deuterated Cyclopentanols.—The opening of epoxide rings with lithium aluminum hydride has been amply demonstrated to be a completely *trans* opening.[6] Consequently, the structure *trans*-cyclopentanol-2-*d* was confidently assigned to the alcohol obtained in good yield from the reaction of cyclopentene oxide with lithium aluminum deuteride. The density of the alcohol indicated 1.0 deuterium/molecule. This material was converted in the usual way to the tosylate (*trans*-II-OTs) which was treated with tetramethylammonium acetate in pure, dry acetone solution. The product, obtained in 76% yield, was assigned the structure of *cis*-cyclopentyl-2-*d* acetate (*cis*-II-OAc) since the reaction conditions were chosen to favor an S_N2 reaction. Hydrolysis gave *cis*-II. The infrared spectra in the 4–11 μ region of *cis*- and *trans*-II and of the corresponding acetates are compared in Table I. The spectra show a number of differences, particularly in the 9–11 μ region. The *cis* and *trans* compounds are not only clearly different and distinguishable, but are not mutually contaminated to any observable extent.

Cyclopentanone-2,2,5,5-d_4 (IV-d_4) was prepared by repeated exchanges of cyclopentanone (IV) with weakly basic D_2O. The infrared spectra of the two ketones showed interesting features. In IV-d_4, the C–D stretching doublet at 2135 and 2230 cm.$^{-1}$ was much less intense than the C–H doublet in IV at 2880 and 2965 cm.$^{-1}$ which is little changed in IV-d_4. Clearly, the intensities of the α-C–H stretching modes are much less than those of the β-C–H, in agreement with Francis[7] that a carbonyl

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[1] This work was communicated in part by A. Streitwieser, Jr., R. H. Jagow and S. Suzuki, This Journal, **77**, 6713 (1955), and by A. Streitwieser, Jr., and R. C. Fahey, *Chemistry & Industry*, 1417 (1957).

[2] This research was supported in part by a grant from the Petroleum Research Fund of the American Chemical Society.

[3] (a) V. J. Shiner, Jr., This Journal, **75**, 2925 (1953); (b) **76**, 1603 (1954).

[4] E. S. Lewis and C. E. Boozer, *ibid.*, **76**, 791 (1954).

[5] For reviews see (a) K. B. Wiberg, *Chem. Revs.*, **55**, 713 (1955), and (b) A. Streitwieser, Jr., *ibid.*, **56**, 571 (1956).

[6] For example, see P. A. Plattner, H. Heuser and M. Feurer, *Helv. chim. Acta*, **32**, 587 (1949); L. W. Trevoy and W. G. Brown, This Journal, **71**, 1675 (1949); W. G. Dauben, R. C. Tweit and R. L. McLean, *ibid.*, **77**, 48 (1955).

[7] S. A. Francis, *J. Chem. Phys.*, **19**, 942 (1951).