(o-, 0.424 v.) > naphthalene (o-, 0.501 v.) > benzene (o-, 0.71 v.).

To summarize: The observed correlation of oxidation-reduction potentials with both the ease and position of ozone attack does offer for the first time, a reasonably consistent explanation why ozone adds predominantly 1,4- to some aromatic compounds and predominantly 1,2- to others.

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Intramolecular Hydrogen Bonding of vic-Diols in Cyclic Systems. II.¹ OH····O and OH \cdots π -Electron Bonding in *cis*- and *trans*-1,2-Diaryl-1,2-acenaphthenediols²

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The syntheses and intramolecularly bonded OH absorption frequencies (3µ region) of a series of cis- and trans-1,2-diary]-1,2-acenaphthenediols are reported in which the 1,2-aryl substituents vary in bulk and electronic effect [Aryl = H (I), phenyl (Ia), 4-methylphenyl (Ib), 2,4-dimethylphenyl (Ic), 2,4,6-trimethylphenyl (Id), and α -naphthyl (Ie)]. In both *cis*-and *trans*-diols, the higher frequency band (3584–3600 cm.⁻¹) is assigned to a weak OH $\cdots \pi$ bond to the naphthalene ring of the acenaphthene system. The lower frequency band (3512–3542 cm.⁻¹) in the *cis*-diols, and the 3544 cm.⁻¹ band in *trans*-I diol are assigned to a stronger OH $\cdots \circ$ O bond between *vic*-OH groups. In the aryl substituted *trans*-diols, the inter-mediate frequency band (3549–3574 cm.⁻¹) is assigned to a OH $\cdots \pi$ electron bond to the aromatic ring of the aryl substituent situated on the adjacent carbon atom.

Introduction

In the first paper of this series,¹ it was found that shifts in the fundamental OH vibrational frequency^a (3μ region) of a series of *cis*- and *trans*-9,10-diaryl-9,10-dihydro-9,10-phenanthrenediols in which the 9,10-diaryl substituents varied in bulk and electronic effects could be interpreted in terms of the non-bonded steric effects of the aryl substituents upon the O-C-C angles at the 9,10-positions.

This paper records and interprets the $\Delta \nu$ (OH) measurements of a series of similarly substituted cis- and trans-1,2-diaryl-1,2-acenaphthenediols.



I, Ar = H

I, AI = II Ia, Ar = phenyl Ib, Ar = 4-methylphenyl (p-tolyl) Ic, Ar = 2,4-dimethylphenyl (m-xylyl) Id, Ar = 2,4,6-trimethylphenyl (mesityl)

ıyl

Ie, Ar =
$$\alpha$$
-naphth

The aryl-substituted trans-diols were prepared by a Grignard reaction^{7-10,22} on acenaphthenequi-

(1) Part I, E. J. Moriconi, F. T. Wallenberger, L. P. Kuhn and W. F. O'Connor, J. Org. Chem., 22, 1651 (1957).

(2) Presented in part at the Meeting-in-Miniature Metropolitan Long Island Subsection, American Chemical Society, New York Section, March, 1958, and at the 134th Meeting of the American Chemical Society, Chicago, Ill., September, 1958.

(3) These concentration independent $\Delta \nu$ (OH) values (in cm.⁻¹) are a direct measure of intramolecular hydrogen bond strength between vic-OH groups; see L. P. Kuhn4-6 for a detailed account of the relationship between molecular structure and intramolecular hydrogen boud formation as measured by $\Delta \nu$ (OH) values.

- (4) L. P. Kuhn, THIS JOURNAL, 74, 2492 (1952).
- (5) L. P. Kuhn, ibid., 76, 4323 (1954).
- (6) L. P. Kuhn, ibid., 80, 5950 (1958).
- (7) S. F. Acree, Am. Chem. J., 33, 186 (1905).
- (8) E. Beschke and M. Kitay, Ann., 369, 200 (1909).
- (9) W. E. Bachmann and E. J. Chu, THIS JOURNAL, 58, 1118 (1936).

none (Table I). The congruent cis-diols (cis-Ia,Ib,Ic,Ie) were synthesized by a magnesium-magnesium iodide, 10-13 or zinc dust-potassium hydroxide^{9,11} reduction of the appropriate 1,8diaroylnaphthalene (Table II) which in turn had been prepared by a lead tetraacetate or potassium dichromate oxidation of the corresponding transdiol (Table III). Unlike their analogs in the phenanthrenediol series, 1,11,12 these methods of syntheses are unequivocal in that the appropriate technique gave only a single isolable isomer.7,13 We were unable to prepare cis-Id diol since all attempts to obtain the intermediate 1,8-di-(2,4,6trimethylbenzoyl)-naphthalene (IId) by either the oxidation of trans-Id diol or the Friedel-Crafts aroylation of mesitylene with naphthalic anhydride were unsuccessful. cis-1,2-Acenaphthenediol (cis-I) was prepared both by the catalytic hydrogenation of acenaphthenequinone¹⁴ and selenium dioxide oxidation of acenaphthene,15 while a lithium aluminum hydride reduction of acenaphthenequinone gave trans-1,2-acenaphthenediol (trans-I)¹⁶ accompanied by a small amount of cis-I.

Experimental

Melting points are uncorrected. Microanalyses were performed by the Schwarzkopf Microanalytical Laboratory, Woodside, N.Y. $\Delta \nu$ (OH) measurements were made with a

(10) (a) P. D. Bartlett and R. F. Brown, ibid., 62, 2927 (1940); (b) R. F. Brown, ibid., 76, 1279 (1954).

(11) M. Gomberg and W. E. Bachmann, ibid., 49, 236 (1927); W. E. Bachmann, ibid., 54, 1969 (1932).

(12) H. C. Fuson and C. Hornberger, Jr., J. Org. Chem., 16, 637 (1951).

- (13) R. C. Fuson and R. O. Kerr, ibid., 19, 373 (1954).
- (14) K. M. Jack and H. G. Rule, J. Chem. Soc., 188 (1938).
- (15) L. Monti, Gazz. chim. ital., 68, 608 (1938); C. A., 33, 1716 (1939).
- (16) L. W. Trevoy and W. G. Brown, THIS JOURNAL, 71, 1675 (1949).

TABLE I

trans-1,2-DIARVL-1,2-ACENAPHTHENEDIOLS

Diol		Reflux time	Recrystn.	Vield.			Cal	Analys	es, % Foun	đ
trans	Ar	hr.	solvent	%	Formula	M.p., °C.	С	н	С	H
Iaª	C ₆ H ₅	3	Hexane	78	$C_{24}\mathrm{H}_{18}\mathrm{O}_{2}$	$156 - 157.5^{\circ}$	85.18	5.36	85.00	5.39
Ib ^{a b}	$4-(CH_3)C_6H_4$	4	(CH ₃) ₂ CHOH	57	$\mathrm{C}_{26}\mathrm{H}_{22}\mathrm{O}_2$	184.5 - 186'	85.22	6.05	85.00	6.00
Ic°	2,4-(CH ₃) ₂ C ₆ H ₃	8	EtOH	16	$C_{28}H_{26}O_2$	153 - 154	85.24	6.64	85.16	6.64
Id°	2,4,6-(CH ₃) ₃ C ₆ H ₂	4	MeOH	10	$C_{80}H_{30}O_2$	197-198	85.27	7.16	85.56	7.18
Ie	α -C ₁₀ H ₇	3	$o - (C1)_2 C_6 H_4^d$	51	$C_{s2}H_{22}\mathrm{O}_2$	208-210 ^g	87.64	5.06	87.57	5.31

^a Acenaphthenequinone was first added to an ice-cold Grignard solution and the mixture was then heated to reflux. ^b Brown's^{10b} technique of distilling off Grignard solvent ether to give a higher reflux temperature was employed. ^c De-scribed in detail in Experimental part. ^d Or acetone-methanol (1.5 l. per g.). ^e Reported^{10b} 158.7-159.0°. ^f Reported^{10b} 185-185.5. ^e Previously isolated as a 1:1 benzene complex, m.p. 142° [E. C. Dodds and W. Lawson, *Proc. Roy. Soc. (Lon-don)*, B125, 222 (1938)].

1,8-DIAROVLNAPHTHALENES

		Reacn.					Analyses, %				
Diketone	Ar	time, min.	Recrysn. solvent	Vield, %	Formula	M.p., °C.	C Cal	ed. H	C	nd H	
IIa	C ₆ H ₅	30	Acetone-alcohol	75°	$\mathrm{C}_{24}\mathrm{H}_{16}\mathrm{O}_2$	$186 - 188^{d}$	85.69	4.79	85.50	4.77	
IIb	$4-(CH_3)C_6H_4$	15	CCl ₄	80°	$C_{26}H_{20}O_2$	183–184°	85.69	5.53	85.60	5.40	
IIc	2,4-(CH ₃) ₂ C ₆ H ₃	60	EtOH	60°	$C_{28}H_{24}O_2$	115 - 117	85.82	6.12	86.06	6.15	
IIeª	α -C ₁₀ H ₇	$30^{b} - 60^{\circ}$	o-Cl2C6H4	60°87 ^b	$C_{32}H_{20}O_2$	237–239 ¹	88.05	4.62	88.21	4.81	
									c 0.11.		

^a Described in detail in Experimental part. ^b Oxidant was lead tetraacetate in acetic acid-benzene. ^c Oxidant was chromic anhydride in acetic acid. ^d Reported⁹ 186.5^o. ^e Reported⁹ 181.5-182.5; 185.0-185.5^o.^{10b} ^f Reported 227-228^o, ref. g, Table I.

Perkin-Elmer model 21 spectrometer equipped with a LiF prism. See ref. 4 for details of sample preparation.

Acenaphthenequinone, yellow needles, m.p. 260-261° from *o*-dichlorobenzene.¹⁷ **1-Acenaphthenol acetate**, originally synthesized from acenaphthene, red lead and acetic acid,¹⁸ was conveniently acenaphthene, red lead and acetic acid,¹⁸ was conveniently prepared by acetoxylation with lead tetraacetate in the following manner: To a solution of 16.2 g. (0.10 mole) of acenaphthene (95%, Eastman No. P 597) in 100 ml. of glacial acetic acid maintained at $60-70^{\circ}$, was added 55.3 g. (0.12 mole) of solid lead tetraacetate (96%, Arapahoe Chemicals Inc. No. 908) in 5-g. portions over a period of 0.5 hour. After a final 15 minutes heating at this same temperature, the dork red viscous solution was poured out 200 ml of water dark red, viscous solution was poured onto 200 ml. of water and the mixture was twice extracted with 15-ml. portions of ether. After the combined extracts were shaken with 100 ml. of a saturated sodium chloride solution, the organic phase was separated, and filtered through a layer of anhydrous sodium sulfate. The solvent was removed under reduced pressure and the crude 1-acenaphthenol acetate was distilled, 164-165° (5 mm.) (bath temp. 180-185°) to yield 17.0 g. (80%) of pure product. 1-Acenaphthenol recrystal-lized from benzene, m.p. 147-149°, was prepared from the alkaline hydrolysis of 1-acenaphthenol acetate¹⁸; lit. m.p. 144.5-145.5°,¹⁸ 146°.¹⁹ The spectral sample of 1-acenaph-thenol was obtained by recrystallizing the product three times from otherapt mp. 149

thenol was obtained by recrystallizing the product three times from ethanol, m.p. 148-149°. *trans*-1,2-Acenaphthenediol (*trans*-I), recrystallized from water, m.p. 149-151, was prepared in 45% yield from ace-naphthenequinone¹⁶; lit.²⁰ m.p. 155-156°. An 8% yield of *cis*-1,2-acenaphthenediol (*cis*-I), m.p. 208.5-209.5° was also obtained.

trans-1,2-Diphenyl-1,2-acenaphthenediol (trans-Ia) and trans-1,2-di-(4-methylphenyl)-1,2-acenaphthenediol (trans-Ib) were prepared according to Bachmann and Chu's,⁹ and Brown's procedure.^{10b} An extension of their techniques gave trans-Ic, trans-Id and trans-Ie (Table I).

trans-1,2-Di-(2,4-dimethylphenyl)-1,2-acenaphthenediol (*trans-Ic*).—The Grignard reagent, prepared under nitrogen from 7.2 g. (0.3 mole) of magnesium turnings, 55.5 g. of 1-bromo-2,4-dimethylbenzene (0.3 mole) and a crystal of io-dine in 175 ml. of anhydrous ether, was refluxed for 30 min-ters and then without cooling particular of 12.2 g. (0.1 utes and then, without cooling, portions of 18.2 g. (0.1

(17) C. S. Marvel and C. F. H. Allen, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 1, report a m.p. of 256-260°.

(19) J. von Braun and O. Bayer, Ber., 59, 920 (1926).

(20) E. H. Charlesworth, H. Campbell, J. J. Conn, C. T. Elston and D. L. Stachiw, Can. J. Chem., 35, 351 (1957).

mole) of dry finely powdered acenaphthenequinone were added, alternating with portions of 200 ml. of dry ben-zene. The mixture was then heated under a gentle reflux with dil hydrochloric acid and ice, the ether layer was separated, dried over anhydrous sodium sulfate, filtered, and after evaporation the resultant oil was digested with abso-lute ethanol to yield crude *trans*-Ic, m.p. 151–154°. One recrystallization from hexane or absolute ethanol gave 6.4 g. of pure trans-Ic (Table I).

trans - 1,2 - Di - (2,4,6 - trimethylphenyl) - 1,2 - acenaph-thenediol (trans-Id).—To approximately 0.1 mole of the icecold Grignard reagent mesitylmagnesium bromide in 80 ml. anhyd. ether prepared in the usual manner²¹ under nitrogen but initiated with a small amount of ethyl bromide instead but initiated with a small amount of etnyl bromide instead of iodine, was added 9.1 g. (0.05 mole) of acenaphthenequi-none; 150 ml. of dry benzene was then added and, with vig-orous stirring, the mixture was refluxed for a period of 3-4 hours. The usual complex hydrolysis and extraction pro-cedure gave an oil which was dissolved in petroleum ether $(30-60^\circ)$; the solution was adsorbed on an alumina column (Woelm's neutral aluminum oxide, activity grade 1), and eluted with 1:2 benzene-petroleum ether $(30-60^\circ)$. Addi-tion of petroleum ether to the eluste curstallized a white tion of petroleum ether to the eluate crystallized a white powder, m.p. $160-170^\circ$; subsequent recystallization from o-dichlorobenzene (10 ml. per g.) gave pure *trans*-Id (Table I).

trans-1,2-(α -Naphthyl)-1,2-acenaphthenediol (trans-Ie). To the refluxing solution of the Grignard reagent 1-naphthylmagnesium bromide in 250 ml. of anhyd. ether prepared from 66.3 g. (0.32 mole) of 1-bromonaphthalene (Eastman No. 46) and 0.30 g. atom of magnesium filings was added in small portions 10.1 g. (0.055 mole) of acenaphthenequinone suspended in 250 ml. of anhyd. ether. The addition was complete in 0.5 hour and the solution was refluxed for an additional three hours. The reaction mixture was then hydrolyzed in 200 g. of ice-20 ml. dil. hydrochloric acid, and the organic phase, after separation, was washed twice with 200 ml. of water, and dried over anhyd. calcium chloride. The ether was carefully evaporated and the oily residue was triturated with ethyl alcohol. The white solid which sep-arated was filtered and recrystallized once from a minimum amount of o-dichlorobenzene (three days) to give pure trans-Ie.

1,8-Dibenzoylnaphthalene (IIa) and 1,8-di-(4-methyl-benzoyl)-naphthalene (IIb) were prepared by a chromic an-hydride-acetic acid oxidation^{9,10} of the appropriate *trans*-

(21) L. I. Smith, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 360.

⁽¹⁸⁾ J. Cason, Org. Syntheses, 21, 1 (1941).

TABLE]	III
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cis-1,2-DIARYL-1,2-ACENAPHTHENEDIOLS

		Reflux						Analy	ses, %	
Diol,		time,	Recrystn.	Yield,	_ .		Cal	ed.	Fo	und
CIS	Ar	hr.	solvent	%	Formula	м.р., °С.	С	н	C	н
Ia^a	C_6H_5	3°	EtOH	25	$\mathrm{C}_{24}\mathrm{H}_{18}\mathrm{O}_2$	$174 - 175^{g}$	85.18	5.36	85.25	5.40
Ib	$4-(CH_3)C_6H_5$	4^{c}	EtOH	90	$C_{26}H_{22}\mathrm{O}_2$	$155 - 156^{h}$	85.22	6.05	85.35	6.15
Ic	$2,4-(CH_3)_2C_6H_4$	12	Petr. ether ^f	53	$C_{28}H_{25}O_2$	156 - 157	85.24	6.64	85.11	6.65
Ie ⁶	α -C ₁₀ H ₇	24^d	$o-(C1)_2C_6H_4$	38	$C_{\mathtt{82}}H_{\mathtt{22}}O_{\mathtt{2}}$	214 - 216	87.64	5.06	87.41	4.94

^a This compound has also been prepared by Bachmann⁹ in 10% yield by sodium amalgam reduction of IIa and by G. Wittig, M. Leo and W. Wiemer [Ber., **64**, 2405 (1931)] via the reduction of IIa with phenylmagnesium bromide. ^b Detailed in Experimental part. ^c The appropriate 1,8-diaroylnaphthalenes were initially added to a warm solution of magnesium-magnesium iodide in anhydrous ether. ^d Reductant was zinc dust-potassium hydroxide mixture in ethanol; see Experimental. ^e Absolute. ^f (30-60°). ^g Reported¹⁰⁸ 177.5-178°. ^h Reported^{10b} 155-156°.

TABLE IV

Frequencies of Free²³ and Intramolecularly Bonded OH Absorption Bands, $\Delta \nu$ (OH) Values, and C-C Bond Distances for Mono- and Dihydric Alcohols in Cyclic Systems

$54 \qquad 1.56^{f}$
54 1.56^{f}
1.54^{23}
61
1.64^{25}
77 ^d
1.54°
39
32
51°

^a Unpublished data graciously supplied to us by Professor R. Criegee, Technische Hochschule, Karlsruhe, Germany. ^b Measurements by Professor P. Schleyer, Princeton University. Preparation of this compound from benzocyclobutadienoguinone and its configurational assignment to be published. We are indebted to Professor M. P. Cava and Mr. R. Pohl for a sample of benzocyclobutadienoquinone [M. P. Cava and D. R. Napier, THIS JOURNAL, **79**, 3606 (1957)]. ^e In Part I of this series, these bands were assigned to a "free" OH absorption. Data presented herein, however, indicate these bands to be more likely due to a OH · · · π electron bond to the aromatic rings. See Ref. 27. ^d Based on the unobserved free OH frequency at 3620 cm.⁻¹ (cyclopentanol) and the observed OH · · · O bonded frequency at 3543 cm.⁻¹. ^e Based on the unobserved free OH frequency at 3618 cm.⁻¹(cyclohexanol) and the observed OH · · · O bonded frequency at 3567 cm.⁻¹. ^f C-C bond length in cyclobutane [J. O. Dunitz and V. Schomaker, J. Chem. Phys., 20, 1703 (1952)]. ^e C-C bond length in cyclohexane [O. Hassel and H. Viervoll, Acta Chem. Scand., 1, 149 (1947)].

diol, while 1,8-di-(2,4-dimethylbenzoyl)-naphthalene (IIc) was obtained via oxidation of *trans*-Ic with lead tetraacetate in acetic acid-benzene (Table II). 1,8-Di-(α -naphthoyl)-naphthalene (IIe) was prepared by both methods. Thus: (a) Chromic Anhydride-Acetic Acid Oxidation. A mix-

(a) Chromic Anhydride-Acetic Acid Oxidation.—A mixture of 0.7 g. (0.0016 mole) of *trans*-Ie and 0.125 g. of chromic anhydride in 10 ml. of glacial acetic acid was heated on a steam-bath for about one hour. The product was precipitated by addition of ice-cold water, filtered, and washed with water to remove the acetic acid. The yellow powder was dried and recrystallized from sodium-dried toluene, or anhydrous methanol (charcoal) to yield IIe as light yellow prisms.

(b) Lead Tetraacetate Oxidation.—A solution of 13.0 g. of 96% lead tetraacetate (0.29 mole) in 200 ml. of 98% acetic acid was carefully prepared by warming the mixture to $50-60^{\circ}$. To this solution was added at once, a solution of 11.5 g. (0.26 mole) of *trans*-Ie in approximately 200 ml. of benzene. The combined solution was permitted to cool to room temperature. Subsequent hydrolysis with 500 ml. of water with vigorous stirring gave a dark brown discoloration of both phases. The organic layer was separated and the solvent evaporated on a steam-bath. The crude product, slightly yellow prisms, were crystallized as in procedure (a) to give 10.0 g. (0.23 mole) of pure IIe.

cis-1,2-Acenaphthenediol (cis-1), m.p. 209-210° from odichlorobenzene was obtained in 6% yield from acenaphthenequinone,¹⁴ and 0.8% yield from acenaphthene¹⁵; lit.²² m.p. 209-210°. cis-1,2-Diphenyl-1,2-acenaphthenediol (cis-Ia) and cis-1,2-di-(4-methylphenyl)-1,2-acenaphthenediol (cis-Ib) were prepared using Brown's procedure.^{10b} An extension of his technique gave the hitherto unreported cis-1,2-di-(2,4dimethylphenyl)-1,2-acenaphthenediol (cis-Ic) and cis-1,2di-(α -naphthyl)-1,2-acenaphthenediol (cis-Ic).

din(α -naphthy)-1,2-acenaphthenediol (cis-le). cis-1,2-Di-(2,4-dimethylphenyl) - 1,2 - acenaphthenediol (cis-lc).—Iodine (0.97 g., 3.82 mmoles) was added under nitrogen all at once to 0.19 g. (7.64 mmoles) of magnesium filings in 10 ml. of anhyd. ether. With continued vigorous stirring, the solution gradually became colorless as the reaction proceeded. After addition of 20 ml. of anhyd. benzene the reaction mass was heated to the boiling point whereupon the heat was removed and two equal portions of IIc (total 1.5 g., 3.82 mmoles) were added, each of which was followed with a 10 ml. of anhyd. benzene wash. The mixture was then refluxed, with stirring, for an additional 6 hours. Upon cooling, the reaction product was decanted from the magnesium into a dil. hydrochloric acid-ice mixture, the mixture was extracted with ether, the ether extracts dried over anhyd. sodium sulfate and, after filtration, evaporated to dryness to yield an oil. This residual oil was digested with absolute ethanol-petroleum ether (30-60°) until crystallization occurred to yield 1.3 g. of crude cis-Ic, light tan flakes.

⁽²²⁾ R. Criegee, L. Kraft and B. Rank, Ann., 507, 194 (1933).

⁽²³⁾ The term "free OH" in vic-diols is, in a literal sense, not the stretching frequency of an unbonded OH, but rather that of the OH group in which the hydrogen is not bonded. However the data herein and those previously reported' indicate the really free OH group in a monohydric alcohol to have approximately the same frequency as the assigned free OH group in vic-diols.



Fig. 1.—Conformations of hydrogen and hydroxyl groups in *cis*- and *trans*-1,2-cyclopentanediols and *cis*- and *trans*-1,2-acenaphthenediols.

Several recrystallizations from petroleum ether $(30-60^\circ)$ gave 0.80 g. of pure *cis*-IIc diol. A mixed m.p. of *cis*-IIc (156-157°) and *trans*-IIc (153-154°) showed a definite depression.

presson: cis-1,2-Di-(α -naphthyl)-1,2-acenaphthenediol (cis-Ie). In general Bachmann's procedure¹¹ was followed: To a mixture of 150 ml. of 90% ethanol and 20 ml. of 40% potassium hydroxide solution was added 10 g. of zinc dust and 3.1 g. (8.0 mmoles) of IIe. The resulting suspension was vigorously refluxed for 24 hours and periodically shaken, after which it was poured onto approximately 200 g. of ice and 8 ml. of glacial acetic acid (to neutralize the solution). Larger acid concentrations lowered the diol yield probably due to rearrangement to the 2,2-di-(α -naphthyl)-acenaphthenone. The resulting white precipitate and zinc dust were filtered off, the residue was washed with water, and air-dried. The organic material was then dissolved and refluxed for 15-30 minutes in 200 ml. of anhyd. benzene. The zinc dust was filtered off and the filtrate was charcoaled (reflux), filtered, evaporated to dryness, and the slightly yellow residue was twice recrystallized from 20-30 ml. of o-dichlorobenzene followed by a cold ethanol wash to yield 1.3 g. of pure cis-Ie. Sodium amalgam,¹¹ and magnesium-magnesium iodide in either ethyl^{106,11} or butyl^{12,13} ether, reductions of IIe were unsuccessful in our hands.

Discussion

 $\Delta \nu$ (OH) values (Table IV) for the 1,2-cyclopentanediols and the 1,2-acenaphthenediols indicate the OH groups to be close together in the cisbut far apart in the trans-conformations (Fig. 1). In the 1,2-cyclopentanediols, there is some evidence that the cyclopentane ring is slightly puckered.^{24,25} In the acenaphthene molecule, however, the planarity of substituents at the 1,8-peri-positions of the naphthalene moiety more probably enjoins the two-carbon-atom bridge to form a planar, fivemembered ring.²⁶ Despite the larger 1,2-C-C bond distance in acenaphthene as compared to cyclopentane (Table IV), the calculated intramolecular ÕH···O bond in cis-1,2-acenaphthenediol $[\Delta\nu(OH) = 79 \text{ cm}.^{-1}]$ is stronger than the observed $OH \cdots O$ bond in *cis*-1,2-cyclopentanediol $[\Delta \nu(OH) = 61 \text{ cm}.^{-1}].$ This can be rationalized simply as the effect of eclipsed OH substituents on

(24) O. Hassel and H. Viervoll [*Tidsskr. Kjemi, Berguesen Met.*, **3**, 31 (1946) *Chem, Abstr.*, **40**, 4580 (1946)] have assumed a plane pentagonal model in their electron diffraction study of cyclopentane and have found the C-C distance to be 1.54 Å. On the basis of a rigorous physical analysis of cyclopentane, however, J. E. Kilpatrick, K. S. Pitzer and R. Spitzer [THIS JOURNAL, **69**, 2483 (1947)] have concluded that a small puckering exists in cyclopentane, and that the angle of maximum puckering rotates around the ring.

(25) The $\Delta\nu(OH)$ value for *cis*-1,2-cyclopentanediol is 61 cm.⁻¹ (Table IV). Since the $\Delta\nu(OH)$ values for *cis*-exo- and *cis*-endobicycloheptanediols are, respectively, 102 cm.⁻¹ and 103 cm.⁻¹ [H. Kwart and W. G. Vosburgh, *ibid.*, **76**, 5400 (1954)], these authors have concluded that the maximum internal hydrogen bond energy is not being realized in *cis*-1,2-cyclopentanediol, and that its ring system must therefore be considerably puckered.

(26) X-Ray analysis [A. I. Kitaigorodoskii, *Zhur. Fiz. Khim.*, 23, 1036 (1949); *Chem. Abstr.*, 44, 897 (1950)] indicates that there is an unusually long bond between these bridge carbon atoms to accommodate the ethane bridge (Table IV).



Fig. 2.—Curves were obtained in CCl₄ solutions at concentrations of approximately 0.005 molar.

the planar *cis*-1,2-acenaphthenediol *versus* skewed OH groups on the puckered *cis*-1,2-cyclopentanediol.

All the *cis*-1,2-acenaphthenediols (Fig. 2) show the presence of two OH absorption bands: the higher frequency, more intense band (3584–3600 cm.⁻¹) assigned to a OH $\cdots \pi$ electron bond to the naphthalene ring,²⁷ and the lower frequency broad band (3512–3542 cm.⁻¹) due to the OH \cdots O bond (Fig. 4a). In the *cis*-1,2-diaryl-1,2-acenaphthene-

(27) That these bands are not free OH absorptions was suggested by Professors P. Schleyer and D. Trifan (private communication, cf., D. S. Trifan, R. Bacskai, P. von R. Schleyer and C. Wintner, Abstr., 135th Natl. Mtg., Am. Chem. Soc., Boston, Mass., April 1959, p. 90-O) and is supported by these observations: (i) bicyclo-[4.2.0]octane-cis-1,2-diol has a free OH absorption band at 3623 cm.⁻¹ When the fused six-membered ring is benzenoid, the high frequency band shifts to 3600 cm.⁻¹ (Table IV). (ii) Similar shifts in cyclopentanol (to acenaphthenol, cis- and trans-1,2-cyclopentanediols (to cis- and trans-1,2-acenaphthenediols), cyclohexanol (to 9,10dihydro-9-phenanthrol), and cis- and trans-1,2-cyclohexanediols (to cis- and trans-9,10-dihydro-9,10-phenanthrenediols) (Table IV). (iii) The observation of Professor R. Schleyer (private communication) that he has encountered no saturated, secondary alcohols that absorb much below 3620 cm.⁻¹



Fig. 3.—Curves were obtained in CCl₄ solution at concentrations of approximately 0.005 molar.

diols, molecular models show that there is considerable steric interference between the two eclipsed bulky aryl substituents. We interpret the increase in intramolecular OH · · · O bond strength in the series cis-I < cis-Ia = cis-Ib < cis-Ie < cis-Ic diols (Table V), as relief of steric strain via an increase of the Ar-C-C bond angles at the 1,2-positions, which at the same time decreases the O-C-C bond angles. As a consequence, the eclipsed vic-OH groups are brought increasingly closer together to form a stronger intramolecular hydrogen bond in the observed order. It is significant that the $\Delta \nu$ (OH) values of the OH \cdots O bond for *cis*-Ia and *cis*-Ib diols, which differ only by a p-methyl substituent, are the same, lending support to the view that the observed effect is predominantly steric. The elec-



Fig. 4.—Conformational diagrams of cis- and trans-1,2diaryl-1,2-acenaphthenediols.

tronic effect of a *p*-methyl substituent should strengthen the internal hydrogen bond by electron release to the ring with consequent increase in repulsive effect between rings. This steric effect also must weaken the OH $\cdots \pi$ bond in the *cis*-aryl substituted diols relative to unsubstituted *cis*-I diol. Finally despite the longer 1,2–C–C bond in the 1,2acenaphthenediols as compared to the probably normal 9,10–C–C bond in the 9,10-dihydro-9,10phenanthrendiols,¹ the higher $\Delta\nu(OH)$ values of the OH \cdots O bond in the former would again seem to indicate the stronger influence of eclipsed over skewed²⁸ conformations. The $\Delta\nu(OH)$ values of the OH $\cdots \pi$ electron bond, respectively, to the naphthalene and biphenyl moieties is significantly the same in both series of aryl-substituted *cis*-diols.

In the trans-1,2-acenaphthenediols (Fig. 3), unsubstituted trans-I diol shows only a strong absorption band at 3600 cm.-1 again assigned to a $OH \cdot \cdot \cdot \pi$ electron bond to the naphthalene ring (Fig. 4b).27 In the trans-1,2-diaryl-1,2-acenaphthenediols, this band appears as a shoulder of increasing intensity in the series: trans-Ia = trans-Ib < trans-Ic < trans-Id. The $\Delta \nu$ (OH) values of the $OH \cdots \pi$ electron bond to the naphthalene ring in this series however are approximately constant (Table V). In this same series, the lower frequency $(3549-3574 \text{ cm}.^{-1})$ bands of the bonded OH are sharper and more intense. Molecular models indicate that in these trans-diols, the two OH groups are at the bottom of a trough, on both sides of which are the two aryl substituents.²⁹ Further, steric

⁽²⁸⁾ A consequence of the approximately 20° angular twist of the two benzene rings required to accommodate the 2,2'-ethane bridge in the 9,10-dihydro-9,10-phenanthrenediol molecule without appreciable distortion [G. H. Beaven, D. M. Hail, M. S. Lesslie and E. E. Turner, J. Chem. Soc., 854 (1952)].

⁽²⁹⁾ R. F. Brown, THIS JOURNAL, 74, 428 (1952).

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$\Delta \nu$ (OH) Values (in Cm. ⁻¹) for <i>cis</i> - A	ND trans-1, DIHVI	2-DIARYL-	1,2-Acenai henanthri	PHTHENEDI ENEDIOLS	OLS AND ci	s- AND tra	ns-9,10-D1	aryl-9,10-
9,10-Phenanthrenediols ^a									
Substituent	OH···πb	оно	OH ···· # b	OH····π [¢]	он…о	$\widetilde{OH}\cdots\pi^{\ell_1}$	оно	OH···π ^e	OH···π ^c
H (I)	36	77	20			13	51	13	
$C_{6}H_{5}(Ia)$	20	93	26	46				16 ⁴	55^{i}
$4-(CH_3)C_6H_4$ (Ib)	20	93	26	52		23	70	170	58^{h}
$2_4 - (CH_3)_2 C_6 H_3 (Ic)$	23	108	24	56		23	79	23	
$2,4,6-(CH_3)_3C_6H_2$ (Id)			26	71		24	93		
α -C ₁₀ H ₇ (Ie)	27	95		52	76	23	86	22	58^{f}

TABLE V

2,4,6-(CH₃)₃C₆H₂ (Id) ... 26 71 ... 24 93 α -C₁₀H₇ (Ie) 27 95 ... 52 76 23 86 22 58^f ^a Based on the unobserved free OH frequency at 3620 cm.⁻¹ (cyclopentanol) and the assigned observed OH $\cdots \pi$ or OH \cdots O bonded frequencies. See discussion. ^b To π electrons of naphthalene moiety. ^c To π electrons of aryl substituents. ^d Based on the unobserved free OH frequency at 3618 cm.⁻¹ (cyclopentanol) and the assigned observed OH $\cdots \pi$ or OH \cdots o bonded frequencies. These data, incidentally should now replace the earlier values.¹ • To π electrons of biphenyl moiety. ^f The $\Delta\nu$ (OH) value previously reported¹ was based on observed OH frequencies of 3596 cm.⁻¹ and 3560 cm.⁻¹ and was ascribed to an OH \cdots O bond between *vic*-OH groups resulting from a preferred conformation. An appealing alternative now discernible is that this bond is an intramolecular OH $\cdots \pi$ electron bond with the aryl substituents, as suggested for all the *trans*-diols reported herein. ^e Based on a very weak band observed at 3601 cm.⁻¹; this band was missed in a previous measurement.¹ ^h Based on a very strong band observed at 3560 cm.⁻¹.

restriction to free rotation of both the aryl and hydroxyl groups increases with the number of omethyl substituents on the aryl moieties. This barrier to free rotation which would limit the motion of the aryl groups to an oscillation about the Ar-C bond, coupled with the opposed but eclipsed conformation of OH and Ar groups, suggests that the OH groups are essentially in the field of the aromatic π electrons of the aryl substituents and that the H of each OH group is bound to the aromatic ring situated on the adjacent carbon atom.³⁰ The sharp, low frequency bands in trans-Ia, trans-Ib, trans-Ic, and trans-Ie diols indicate the major fraction of these molecules at equilibrium to have the $OH \cdots \pi$ electron bonded structure to the aromatic ring of the aryl substituent (Fig. 4c).³¹ In trans-Id diol, the balance between steric and electronic effects shifts the equilibrium so that more of this sample exists in this bonded form. Since the sharp, intense high frequency band (3568 cm.-1) of trans-Ie diol is in the same region as the OH $\cdots \pi$ electron bonded (to the aryl substituent) frequencies of trans-Ia to trans-Id diols, it has received the same assignment. This suggests that the only other stretching frequency observed (3544 cm, -1) is due

(30) A possible but less likely alternative: intramolecular OH... π electron bonding between hydroxyl group and aryl substituent on the same carbon atom.

(31) Such intramolecular interaction $(3\mu \text{ region})$ previously has been reported: (a) in β -mesityl-substituted vinyl alcohols [A. M. Buswell, W. H. Rodebush, and R. McL. Whitney, THIS JOURNAL, **69**, 770 (1947); (b) in α -hydroxyethylferrocene, 1,2-di- α -hydroxyethylferrocene and phenethyl alcohol [D. S. Trifan, J. L. Weinman and L. P. Kuhn, *ibid.*, **79**, 6566 (1957)]; (c) in the first overtone of the OH fundamental stretching vibration (1.5 μ region) for phenethyl alcohol, pmethoxyphenethyl alcohol, 1,2-diphenylethanol and 1-phenyl-2propanol [I. M. Goldman and R. O. Crisler, J. Org. Chem., **23**, 751 (1958)]; (d) in o-phenylphenol [A. W. Baker and A. T. Shulgin, THIS JOURNAL, **30**, 5358 (1958)]; (e) in phenyl substituted aliphatic alcohols [P. von R. Schleyer, D. S. Trifan and R. Bacskai, *ibid.*, **80**, 6691 (1958)]. to the intramolecular hydrogen bond between vic-OH groups (Fig. 4d).^{32,33}

This assumption of intramolecular hydrogen bonding to the π electrons of the aryl substituents, for these vic-trans-diols would account for: (i) the type and intensity of absorption bands observed. (ii) the lack of any such internal hydrogen bond in *trans*-I diol; (iii) the presence of such an internal hydrogen bond in all aryl-substituted trans-diols despite the unfavorable conformation (Fig. 1); (iv) the increase of internal hydrogen bond strength in the series: trans-Ia < trans-Ib < trans-Ic < trans-Ic Id which then can be rationalized in terms of electron-release to the ring by o- and p-methyl substituents; (v) the absence of any electronic effect between cis-Ia and cis-Ib diols, and the stronger OH · · · O bond in the series: cis-I < cis-Ia =cis-Ib < cis-Ie < cis-Ic which has been interpreted predominantly in terms of steric effects.

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(32) Similar assignments have been made by D. S. Trifan, J. L. Weinman and L. P. Kuhn (see ref. 31b) for the homoannular 1,2-di- α -hydroxyethylferrocene.

(33) A referee has noted a "poorly defined peak at about 3544 cm."'' in *trans*-Ic diol and has suggested an alternative view that the 3544-3549 cm." and 3564-3574 cm." bands are the result of two bonded conformations in which the aryl substituents are rotated 180° apart. This suggestion has merit, but it should also be noted that such constrained bonds usually appear as shoulders, and at least in *trans*-Id diol, the 3549 cm." band is quite sharp.

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