basic amines with Schiff bases derived from strongly basic amines.[29] The principal goal of the present studies was to provide additional evidence for this conclusion. Methoxyamine ($pK_a = 4.60$) is about as basic as aniline ($pK_a = 4.58$). Thus, by varying the nature of the polar substituent in the aniline moiety of N-benzylideneanilines, one may make the resident amine either more or less basic than the attacking amine, methoxyamine. Provided that the relative basicities of the resident and attacking amine is the only important factor in determining the behavior of the *gem*-diamine intermediates, one expects that the attack of methoxyamine on those substrates possessing electron-donating substituents will be rate determining and that decomposition of the tetrahedral intermediate will be rate determining for those substrates possessing electron-withdrawing substituents. Thus a transition in rate-determining step with variation in polar substituent is expected for the methoxyaminolysis of N-benzylideneanilines, and it was hoped that such behavior would manifest itself in the form of a break in the Hammett plot. Such is not the case. Either no transition in rate-determining step occurred or else the effect of polar substituents on the rate constants is the same in both cases. Inasmuch as previous work suggests that the latter alternative is not unlikely,[29] and since the assumption that basicity alone determines the rate-determining step is certainly oversimplified, no grounds exist for distinguishing between these alternatives.

**Acknowledgment.** We are indebted to Professors William P. Jencks, C. Gardner Swain, Edward Thornton, and Richard Schowen for helpful comments concerning certain aspects of this work.

# Conformational Mobility and Optical Rotation Effects of Aromatic Nuclei[1]

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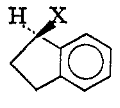
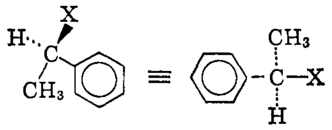
*Contribution from the Department of Chemistry, Purdue University, Lafayette, Indiana. 47907.* *Received November 17, 1965*

**Abstract:** A series of 1-substituted indans has been prepared in known absolute configuration. Multiple Cotton effects are shown in the region 250–275 mμ, corresponding in fine structure to the $^1L_b$ absorptions bands, notably when the 1 substituent has a positive charge or can hydrogen bond to the nucleus. The dispersion curves of the indans are essentially enantiomeric to those of the corresponding α-phenylethyl compounds of the same absolute configuration; the open-chain compounds show much smaller Cotton effects. These results indicate that conformational mobility has a significant effect on the optical rotation properties of aromatic compounds.

Desiring to gain some insight into the effect of conformational mobility of the phenyl group upon the optical rotation properties of aromatic compounds, we have prepared a series of 1-substituted indans (Ia–h), in the absolute configuration shown, for comparison with the corresponding open-chain compounds (II). As may be seen from the figures, many, but not all, of these compounds show multiple rotation anomalies in the region of the $^1L_b$ transition[3] of the aromatic ring. These are similar to, but in several cases larger than, apparently authentic anomalies which have recently been reported for other aromatic compounds.[4] We believe that we have taken the precautions necessary[5] to ensure that these anomalies are real and not artifacts.



I



II

a, X = $CO_2H$
b, X = $CO_2Na$
c, X = $NH_2$
d, X = $NH_3Cl$
e, X = $N(CH_3)_3I$
f, X = OH
g, X = $CH_2OH$
h, X = $CH_3$

The substituted indans were all prepared from ($R$[6])-(+)-1-indancarboxylic acid[7] (Ia) by standard synthetic

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[1] A Useful Model of Optical Activity. VII. Part VI: J. H. Brewster and J. E. Privett, *J. Am. Chem. Soc.*, **88**, 1419 (1966).

[2] We wish to express our appreciation to the Purdue Research Foundation and the Eli Lilly Co. for grants in support of this research and to the National Science Foundation for Grant GP1688 for purchase of the spectropolarimeter.

[3] J. R. Platt, *J. Chem. Phys.*, **17**, 484 (1949).

[4] (a) G. G. Lyle, *J. Org. Chem.*, **25**, 1779 (1960); (b) I. P. Dirkx and Th. J. DeBoer, *Rec. Trav. Chim.*, **83**, 535 (1964); (c) K. S. Brown, Jr., and C. Djerassi, *J. Am. Chem. Soc.*, **86**, 2456 (1964); (d) T. M. Hooker, Jr., and C. Tanford, *ibid.*, **86**, 4989 (1964); (e) L. Verbit, *ibid.*, **87**, 1617 (1965); (f) A. Moscowitz, A. Rosenberg, and A. E. Hansen, *ibid.*, **87**, 1813 (1965); (g) A. R. Battersby, I. R. C. Bick, W. Klyne, J. P. Jennings, P. M. Scopes, and M. J. Vernengo, *J. Chem. Soc.*, 2239 (1965); (h) A. Yogev and Y. Mazur, *Chem. Commun.*, 388 (1965).

[5] A Bendix-Ericsson Polaromatic-60 recording spectropolarimeter with a 250-w xenon light source was used. Concentrations were chosen so that transmission did not drop below 40% in the spectral regions of interest. Under these conditions further dilution did not alter the shape of the dispersion curve, enantiomers gave mirror image curves, and racemic substances gave zero rotation; see I. P. Dirkx, P. J. vander Haak, and F. J. L. Sixma, *Anal. Chem.*, **36**, 1988 (1964), and C. Djerassi, E. Lund, E. Bunnenberg, and J. C. Sheehan, *J. Org. Chem.*, **26**, 4509 (1961), for discussions of some factors which produce false anomalies in strongly absorbing solutions.

[6] R. S. Cahn, C. K. Ingold, and V. Prelog, *Experientia*, **12**, 81 (1956); R. S. Cahn, *J. Chem. Educ.*, **41**, 116 (1964).

[7] A. Fredga, *Chem. Ber.*, **89**, 322 (1956), has assigned the $R$ configuration to (+)-Ia by the method of quasiracemates. W. G. Dauben and P. Baumann, *Tetrahedron Letters*, 565 (1961), have assigned the $R$

methods. Thus (+)-Ia, 91% optically pure, was reduced to the (*R*)-(+)-carbinol (Ig)[8] and this, by way of its *p*-toluenesulfonate, was reduced to the (*R*)-(−)-methyl compound (Ih), lithium aluminum hydride being used in both cases. A portion of the sample of the (+)-acid (Ia) was converted to the (*R*)-(−)-methyl ketone by reaction with methyllithium[9] and this was converted to the (*R*)-(+)-acetate by oxidation with perbenzoic acid,[7,9b] saponification giving (*R*)-(−)-1-indanol of about 86% optical purity.[10] (*R*)-(−)-1-Indanamine (Ic) was obtained from the (*R*)-(+)- acid *via* the Curtius reaction;[11] the optical purity of the acid used in this preparation was low. The N-methyl derivative was obtained by lithium aluminum hydride reduction of the formamide, while the N,N-dimethyl derivative was obtained by methylation with formaldehyde and formic acid.[12] The quaternary salt (Ie) could be prepared from the tertiary amine, or directly from the primary amine with methyl iodide.[13] All of the compounds described above were obtained in racemic form in the course of pilot experiments. The infrared spectra of the racemic and active substances were routinely compared and in every case were essentially identical. All of the rotatory dispersion curves[5] have been corrected to optical purity.

## Experimental Section[14]

**Indene-3-carboxylic acid**[15] was prepared by the procedure of Cromwell and Capps[16] in which carbon dioxide is added to indenyllithium prepared by the reaction of indene with *n*-butyllithium, mp 159–160° (lit.[17] mp 159.5–161°).

**1-Indancarboxylic Acid.** The sodium salt of indene-1-carboxylic acid was hydrogenated using W-2 Raney nickel catalyst[18] as done by Wunderlich.[19] The reduced acid was dissolved out of the tarry residue by digestion with petroleum ether (bp 35–37°). The reduced acid had mp 55–56° (lit.[20] mp 56.5–57°); nmr spectrum ($CDCl_3$), δ 2.10–3.20 (4 H, methylene), 4.07 (1 H, tertiary as triplet), and 7.25 (4 H, aromatic). The amide, prepared by reaction of ammonia with indancarboxylic acid chloride, gave white needles, mp 160–161° (lit.[17] mp 162–163°), after recrystallization from ethanol.

**Resolution of 1-Indancarboxylic Acid.** The resolution of the acid was carried out *via* its brucine salt following the procedure of Fredga.[7] Fractional crystallization occurred more slowly than had been reported and only after evaporation of about 10% of the specified volume of mixed acetone–water solvent. Upon decomposition of the brucine salt and subsequent purification, (*R*)-(+)-acid, mp 45°, was obtained with $[\alpha]^{29}_{D}$ +39.2° (*c* 1.72, benzene). The rotation corresponded to an optical purity of 91% based on the value given by Fredga[7] of $[\alpha]^{29}_{D}$ +43.3° (*c* 2.59, benzene) for the optically pure acid; RD in isooctane (*c* 0.028) showed $[M]^{24}_{588}$ +59.3°, $[M]_{272}$ +862° (peak), $[M]_{266}$ +528° (trough), $[M]_{264}$ +640° (peak), $[M]_{256}$ +486° (trough), $[M]_{238}$ +1270°; RD in methanol (*c* 0.023) showed $[M]^{24}_{556}$ +12.3°, $[M]_{272}$ +503° (peak), $[M]_{266}$ +321° (trough), $[M]_{263}$ +486° (peak), $[M]_{256}$ +428° (trough), $[M]_{238}$ +1650°; RD of sodium salt in water (*c* 0.017) showed $[M]^{24}_{588}$ +75.5°, $[M]_{294}$ +429°, $[M]_{250}$ +2000°, $[M]_{238}$ +3940°.

**1-Indanylcarbinol.** To 11.3 g (0.030 mole) of lithium aluminum hydride in 25 ml of dry ether, 4.0 g (0.025 mole) of 1-indancarboxylic acid dissolved in 25 ml of ether was added dropwise with stirring. After 2.5 hr, dilute hydrochloric acid was added to decompose the excess hydride; the mixture was stirred until the precipitated salts had dissolved. The ether layer was removed and the aqueous layer was extracted twice with ether. The combined organic materials were dried over magnesium sulfate. The ethereal solution was concentrated to a yellow oil that gave, upon distillation, 3.1 g (84%) of carbinol, bp 75–78° (3 mm). The infrared spectrum indicated that the product was an alcohol, $\lambda_{max}$ 3.0 and 9.75 μ.

(*R*)-(+)-**1-Indanylcarbinol.** This compound was prepared in 91% yield in the above manner from 1-indancarboxylic acid ($[\alpha]^{29}_{D}$ +39.2°). A portion of this material was purified further by vpc with a Craig polysuccinate preparative column.

*Anal.* Calcd for $C_{10}H_{12}O$: C, 81.04; H, 8.16. Found: C, 80.85; H, 8.32.

The optical purity of the 1-indanylcarbinol used in the study below was 91%; RD in isooctane (*c* 0.017) showed $[M]^{24}_{588}$ +27.0°, $[M]_{272}$ +933° (peak), $[M]_{270}$ +412° (trough), $[M]_{268}$ +548° (peak), $[M]_{256}$ + 182° (trough), $[M]_{238}$ +1240°.

**1-Indanylcarbinyl *p*-Toluenesulfonate.** The general procedure of Ham[21] was followed. To a solution of 2.0 g (0.013 mole) of indanylcarbinol in 13 ml of anhydrous pyridine at −5° was added 3.82 g (0.020 mole) of *p*-toluenesulfonyl chloride. The reaction mixture was kept at 0° for 48 hr and then poured into 50 ml of water. Three extractions with ether were followed by washing of the combined extracts with cold dilute hydrochloric acid, water, and finally sodium bicarbonate solution. The solution was dried over magnesium sulfate and the solvent was then removed to give 2.9 g (74%) of an oil. This material was induced to crystallize in petroleum ether (bp 35–37°), giving colorless plates, mp 34–35°.

*Anal.* Calcd for $C_{17}H_{18}SO_3$: C, 67.54; H, 6.00. Found: C, 67.82; H, 6.25.

(*R*)-**1-Indanylcarbinyl *p*-Toluenesulfonate.** The active tosylate was prepared and purified by the method used for the racemic compound. Long, rectangular plates, mp 47–48°, were obtained in 63% yield. The infrared spectrum was identical with that of the

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configuration to (−)-1-indanol (If) by an ingenious argument based on their studies of the structure of suprasterol II. (See C. P. Saunderson and D. C. Hodgkin, *Tetrahedron Letters*, 573 (1961), for a simultaneous determination of the structure of suprasterol II.) The conversion of (+)-Ia to (−)-If shows that these two assignments are consistent. After our work had been completed, D. Battail and D. Gagniere, *Bull. Soc. Chim. France*, 3076 (1964), reported the conversion of (+)-Ia to (−)-If by essentially the method reported here.

(8) The racemic carbinol has usually been prepared by hydrogenation of hydroxymethylindene; see A. J. Davidson and R. O. C. Norman, *J. Chem. Soc.*, 5415 (1964); R. Huisgen and G. Seidl, *Chem. Ber.*, **96,** 2744 (1963). It has recently been prepared by the method used here: A. L. Goodman and R. H. Eastman, *J. Am. Chem. Soc.*, **86,** 908 (1964).

(9) (a) C. Tegner, *Acta Chem. Scand.*, **6,** 782 (1952); (b) K. Mislow and J. Brenner, *J. Am. Chem. Soc.*, **75,** 2318 (1953); K. Mislow and C. L. Hamermesh, *ibid.*, **77,** 1590 (1955). Mislow and his co-workers converted optically active alkylphenylacetic acids to active ketones by this method; partial racemization occurred unless ammonium chloride solution was used in the hydrolysis step. In the present series the ketone has a very small rotation: a sample with $[\alpha]_{D}$ −1.60° in isooctane gave (−)-indanol of about 86% optical purity.

(10) Based on the value, $[\alpha]^{20}_{D}$ +34.4° (*c* 1.97, $CHCl_3$), for resolved indanol: W. Hückel and F. Mossner, *Ann.*, **637,** 57 (1960).

(11) J. Kenyon and D. P. Young, *J. Chem. Soc.*, 263 (1941).

(12) R. N. Icke, B. B. Wisegarver, and G. A. Alles, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p 723.

(13) F. S. Kipping and H. Hall, *J. Chem. Soc.*, **77,** 469 (1900).

(14) All melting points are uncorrected. Microanalyses were performed by Dr. C. S. Yeh and Mrs. M. Hudgens. Infrared spectra were recorded on Perkin-Elmer Models 21 and 221 spectrophotometers by Miss S. Hall and on a Perkin-Elmer Infracord Model 137B spectrophotometer. Ultraviolet spectra were recorded on the Bausch and Lomb Model 505 spectrophotometer by Miss S. Hall. Nuclear magnetic resonance spectra were recorded on the Varian A-60 by Mr. W. Baitinger; peak positions are reported in ppm from tetramethylsilane (δ). Vapor phase chromatography (vpc) was carried out on an Aerograph fractometer Model A-90-C, using helium as the carrier gas. Specific rotations were determined on a Zeiss polarimeter. Rotatory dispersion (RD) data were recorded on an automatic recording spectropolarimeter, the Bendix-Ericsson Polaromatic 60. A xenon 250-w light source was used and the sensitivity of the instrument ranged from 0.0002° at 546 mμ to 0.0019° at 200 mμ. The slit width was set at 1.0 mm throughout the scanning. A standard three-piece cell with quartz end plates was used. The concentration (*c*) is expressed as grams per 100 ml of solvent. Values for wave numbers shown on the charts are in kilokaysers (kK) and should be multiplied by $10^3$ to convert to $cm^{-1}$ or divided into $10^4$ to convert to mμ.

(15) A. Melera, M. Claesen, and H. Vanderhaeghe, *J. Org. Chem.*, **29,** 3705 (1964), show that the substance named as the 1-acid by earlier workers is, in fact, the 3-acid.

(16) N. H. Cromwell and D. B. Capps, *J. Am. Chem. Soc.*, **74,** 4448 (1952).

(17) W. S. Knowles, J. A. Kuck, and R. C. Elderfield, *J. Org. Chem.*, **7,** 377 (1942).

(18) R. Mozingo, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p 181.

(19) W. Wunderlich, *Arch. Pharm.*, **286,** 512 (1953).

(20) M. Tiffeneau and A. Orekhoff, *Bull Soc. Chim. France*, **27,** 789 (1920).

(21) G. E. Ham, Ph.D. Thesis, Purdue University, 1956.

racemic compound. The compound exhibited a tendency to discolor on standing.

**1-Methylindan.** To 0.5 g (0.014 mole) of lithium aluminum hydride in 25 ml of dry ether was added 1.0 g (0.03 mole) of the above tosylate. The solution was stirred overnight and then the excess hydride was decomposed. The organic layer was separated and the aqueous layer was extracted with ether. Drying over magnesium sulfate was followed by removal of solvent to give a colorless oil, bp 184–186° (lit.[22] bp 182–183°), in 0.25-g yield (57%); nmr spectrum ($CCl_4$), δ 1.25 and 1.35 (3 H, methyl), 1.75–3.05 (4 H, methylene), 3.30 (1 H, tertiary as triplet), and 7.21 (4 H, aromatic). The infrared spectrum was identical with a published one (API 1599).

**(*R*)-(−)-1-Methylindan.** This compound was prepared by the procedure used for the racemic hydrocarbon; it was purified by vpc with the Craig polysuccinate preparative column.

*Anal.* Calcd for $C_{10}H_{12}$: C, 90.85; H, 9.15. Found: C, 91.15; H, 9.31.

The optical purity of the 1-methylindan studied below was 91% based on the starting acid, $[\alpha]^{29}\mathrm{D}$ +39.2°; RD in isooctane (*c* 0.024) showed $[M]^{24}_{556}$ −10.2°, $[M]_{500}$ −24.1°, $[M]_{455}$ −23.7°, $[M]_{313}$ −23.2°, $[M]_{294}$ −5.40°, $[M]_{278}$ −57.0°, $[M]_{263}$ −103°, $[M]_{250}$ −104°, $[M]_{238}$ −110°, $[M]_{232}$ −50.9.

**1-Indanyl Methyl Ketone.** The general procedure of Tegner[9a] was modified somewhat. The method called for a dropwise addition of a twofold excess of methyllithium (from methyl iodide and lithium) to an ethereal solution of carboxylic acid with subsequent reflux of 30 min. However a 10-min addition time for a fourfold excess of methyllithium to the 1-indancarboxylic acid solution followed by a 10-min period of stirring was found to be the optimum condition for a good yield (60–80%) of ketone, bp 80–84° (2 mm); infrared spectrum with $\lambda_{\max}$ 5.90, 7.40, 8.60, and 13.25 μ; nmr spectrum ($CCl_4$) δ 1.90–3.10 (4 H, methylene), 2.05 (3 H, methyl), 4.92 (1 H, tertiary as triplet), and 7.15 (4 H, aromatic). The semicarbazone was recrystallized from methanol, mp 143–144°.

**(*R*)-(−)-1-Indanyl Methyl Ketone.** The usual preparative procedure for the ketone was followed with starting material, 1-indancarboxylic acid ($[\alpha]^{29}\mathrm{D}$ +39.2°), giving a crude yield of 69% of the desired product. Purification by vpc was performed using a Craig polysuccinate preparative column. The amount of side products was estimated to be about 5% by vpc.

*Anal.* Calcd for $C_{11}H_{12}O$: C, 82.46; H, 7.55. Found: C, 81.98; H, 7.66.

The optical purity of the ketone based on data from (*R*)-(−)-1-indanol (below) is about 86%; RD in isooctane (*c* 0.71, 588–357 mμ; *c* 0.20, 357–238 mμ) showed $[M]^{24}_{588}$ −2.80°, $[M]_{333}$ −43.5°, $[M]_{318}$ −362° (trough), $[M]_{313}$ −204° (peak), $[M]_{307}$ −346° (trough), $[M]_{275}$ +1820° (peak), $[M]_{256}$ −41.8° (trough), $[M]_{238}$ +508°.

**1-Indanyl Acetate.** The method of Mislo wand Brenner[9b] was used for the preparation of 1-indanyl acetate. Since only 1.60 g (0.01 mole) of 1-indanyl methyl ketone was to be oxidized by perbenzoic acid, a shorter reaction time of 36 hr was found to be advisable, thus preventing further oxidation of the ester to indanone-1. A sweet-smelling oil was obtained in a yield of 1.50 g (85%), bp 75–79° (1 mm). The unreacted ketone (5–10%) was removed by vpc fractionation using the Craig polysuccinate preparative column. The infrared spectrum of the ester had $\lambda_{\max}$ at 5.82, 7.35, 8.05, and 13.35 μ; nmr spectrum ($CCl_4$) δ 1.90–3.05 (4 H, methylene), 1.95 (3 H, methyl), 6.10 (1 H, tertiary as triplet), 7.18 (4 H, aromatic).

**(*R*)-(+)-1-Indanyl Acetate.** Using the methyl ketone prepared from 1-indancarboxylic acid ($[\alpha]^{29}\mathrm{D}$ +39.2°), 1-indanyl acetate was obtained in 62% crude yield. During the vpc fractionation with the Craig polysuccinate column, a small amount of indene was detected; this presumably was formed by elimination of acetic acid from indanyl acetate.

*Anal.* Calcd for $C_{11}H_{12}O_2$: C, 74.97; H, 6.86. Found: C, 75.79; H, 6.96.

The error in the carbon and hydrogen analyses may be attributed to a slight contamination (6%) of the vpc sample by indene. The ester has an optical purity of 86% based on the value found for the optical purity of (*R*)-(−)-1-indanol;[10] RD in isooctane (*c* 0.025) showed $[M]^{24}_{588}$ +76.5°, $[M]_{272}$ +1360° (peak), $[M]_{269}$ +982° (trough), $[M]_{266}$ +1250° (peak), $[M]_{263}$ +1000° (trough), $[M]_{238}$ +3520°; RD in methanol (*c* 0.022) showed $[M]^{24}_{500}$ +91.2°, $[M]_{272}$ +200° (peak), $[M]_{270}$ +1460° (trough), $[M]_{266}$ +1730° (peak), $[M]_{263}$ +1410° (trough), $[M]_{238}$ +4300°.

**1-Indanol.** To 0.5 g of potassium hydroxide in 4 ml of water was added 0.5 g (0.028 mole) of 1-indanyl acetate in 9 ml of methanol. The solution was heated at reflux for 90 min, then cooled, diluted with water, and extracted with ether. The ether was dried over magnesium sulfate and the solvent was removed to give a yellow oil. This was purified by vpc using a silicone GE-SF 96 column to give 0.3 g (79%) of 1-indanol, mp 49–50° (lit.[23] mp 54°). The infrared spectrum of the solid was identical with that published by Hückel[10] for indanol.

**(*R*)-(−)-1-Indanol.** The previously mentioned saponification procedure was modified by allowing the mixture to stand at room temperature for 24 hr. The usual work-up was followed by vpc fractionation using the silicone GE-SF 96 analytical column. The white solid, 1-indanol, mp 48–49°, had an infrared spectrum very similar to that of the racemic compound. There were differences in intensities of absorption, but not location, at 7.75 and 9.80 μ; nmr spectrum ($CDCl_3$) δ 1.75–3.05 (4 H, methylene), 1.92 (1 H, hydroxyl), 5.20 (1 H, tertiary as triplet), 7.25 (4 H, aromatic).

*Anal.* Calcd for $C_9H_{10}O$: C, 80.56; H, 7.51. Found: C, 80.52; H, 7.18.

RD in isooctane (*c* 0.022) showed $[M]^{24}_{556}$ −17.0°, $[M]_{278}$ −104°, $[M]_{272}$ +571° (peak), $[M]_{269}$ −250° (trough), $[M]_{265}$ +29.4° (peak), $[M]_{238}$ −1090°; RD in methanol (*c* 0.023) showed $[M]^{24}_{556}$ −40.5°, $[M]_{385}$ −48.4°, $[M]_{313}$ 0°, $[M]_{272}$ +660° (peak), $[M]_{269}$ +53.9° (trough), $[M]_{264}$ +296° (peak), $[M]_{250}$ −415°, $[M]_{238}$ −340°.

Using the data of Hückel[10] for resolved indanol ($[\alpha]^{20}\mathrm{D}$ +34.4° (*c* 1.97, chloroform)) as the value for the optically pure compound, the (*R*)-(−)-1-indanol ($[\alpha]^{24}\mathrm{D}$ −29.6° (*c* 1.35, chloroform)) obtained above has an optical purity of 86%.

**Hydrocinnamic Acid.** Cinnamic acid was hydrogenated following the method in Vogel,[24] with the addition of a small amount (0.25 ml) of glacial acetic acid. Hydrocinnamic acid was obtained quantitatively, mp 46–47° (lit.[25] mp 47–48°).

**Indanone-1.** A mixture of 11 g of thionyl chloride and 11 g (0.073 mole) of hydrocinnamic acid was allowed to stand overnight before the excess thionyl chloride was removed under reduced pressure. The acid chloride was mixed with 50 ml of dry petroleum ether (bp 50–60°) and cooled in ice. To this was added 11 g of aluminum chloride in small portions with shaking. After termination of the addition, the mixture was heated to reflux and then cooled. Decomposition and dissolution of the salts was effected by addition of ice followed by concentrated hydrochloric acid. The mixture was steam distilled and the distilled ketone was taken up in ether. Upon drying and removal of solvent, 6.6 g (71%) of a yellow solid, mp 36–38° (lit.[26] mp 41–42°), was obtained.

**Indanone 1-Oxime.** The procedure of Kipping gave the oxime in 88% yield, mp 138–140° (lit.[26] mp 140°).

**1-Indanamine Hydrochloride.** The method of Levin[27] employing an activated Pd-C catalyst with additional $PdCl_2$ in the presence of hydrochloric acid was used for the reduction of indanone oxime (4.4 g) to give 5.25 g (93%) of 1-indanamine hydrochloride, mp 208–210° (lit.[28] mp 208°).

**1-Indanamine Hydrochloride *via* the Curtius Reaction.** Indancarboxylic acid chloride was prepared by the overnight reaction of 1.0 g (0.0060 mole) of 1-indancarboxylic acid in 10 ml of thionyl chloride at room temperature with subsequent removal of unreacted thionyl chloride under reduced pressure. The acyl chloride was added to a suspension in ether (2.0 g) of powdered dried sodium azide (freshly precipitated by acetone from a minimal amount of water).[11] After 24 hr of stirring, followed by removal of unreacted azide, the ether solution was heated on a steam bath until only an oil remained. Benzene was added and the heating was repeated. Then 10 ml of concentrated hydrochloric acid was added and the mixture was heated at reflux for several hours. The acid solution was cooled, extracted with ether, and evaporated to dryness. The indanamine hydrochloride was recrystallized from methanol and was obtained in 63% yield (0.66 g), mp 205–207° (lit.[28] mp 208°). The infrared spectrum was identical with that of the hydrochloride reported above.

1-Indanamine was regenerated in basic solution, extracted into ether, and obtained by distillation, bp 222–224° (lit.[22] bp 220°);

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(22) J. von Braun and E. Danziger, *Ber.*, **50**, 56 (1917).

(23) R. Weissgerber, *ibid.*, **44**, 1445 (1911).

(24) A. I. Vogel, "Practical Organic Chemistry," 3rd ed, Longmans, Green and Co., New York, N. Y., 1956, p 191.

(25) E. Schwenk and D. Papa, *J. Org. Chem.*, **11**, 798 (1946).

(26) F. S. Kipping, *J. Chem. Soc.*, **65**, 480 (1894).

(27) N. Levin, B. E. Braham, and H. G. Kolloff, *J. Org. Chem.*, **9**, 380 (1944).

(28) A. Konig, *Ann.*, **275**, 348 (1893).

nmr spectrum ($CDCl_3$) $\delta$ 1.75–3.05 (4 H, methylene), 2.70 (2 H, amine), 4.35 (1 H, tertiary as triplet), 7.25 (4 H, aromatic).

**(*R*)-(−)-1-Indanamine.** The amine hydrochloride was prepared from 1-indancarboxylic acid ($[\alpha]^{27}\mathrm{D}$ +11.0°), optical purity 25%, using the Curtius procedure described for the preparation of the *dl* compound. The yield of amine hydrochloride, mp 204–206°, was 58%.

The amine, of optical purity 25%, was released from the salt as needed in a basic solution and purified by vpc using a silicone GE-SF 96 column.

*Anal.* Calcd for $C_9H_{11}N$: C, 81.16; H, 8.33. Found: C, 81.48; H, 8.25.

RD in isooctane (*c* 0.035) showed $[M]^{24}_{556}$ −15.7°, $[M]_{313}$ −42.8°, $[M]_{272}$ +33.6° (peak), $[M]_{267}$ −70.5° (trough), $[M]_{263}$ −7.31° (peak), $[M]_{238}$ −831°; RD in methanol (*c* 0.025) showed $[M]_{556}$ −18.2°, $[M]_{294}$ −107°, $[M]_{272}$ +37.8° (peak), $[M]_{268}$ −97.0° (trough), $[M]_{265}$ 0° (peak), $[M]_{250}$ −356°, $[M]_{238}$ −304°.

RD of amine hydrochloride in methanol (*c* 0.485, 588–294 m$\mu$; *c* 0.045, 294–238 m$\mu$) showed $[M]_{588}$ −6.55°, $[M]_{377}$ 0°, $[M]_{272}$ +237° (peak), $[M]_{270}$ +171° (trough), $[M]_{266}$ +176° (peak), $[M]_{256}$ 0° (trough), $[M]_{238}$ +205°.

**N-Formyl-1-indanamine.** The amine liberated from 0.17 g of indanamine hydrochloride was combined with 1 ml of 90% formic acid and 5 ml of toluene. Distillation of the azeotrope gave an oily residue which crystallized in water to give white needles, mp 89–91°, in 0.1 g yield (63%).

*Anal.* Calcd for $C_{10}H_{11}ON$: C, 74.6; H, 6.84; N, 8.70. Found: C, 74.42; H, 6.95; N, 8.79.

**(*R*)-N-Formyl-1-indanamine.** The active compound was prepared in the same manner as the racemic compound. Using 1-indanamine prepared from acid $[\alpha]^{27}\mathrm{D}$ +23.6°), white crystals, 0.3 g (60%), were isolated with mp 94–95° (recrystallized from water).

**N-Methyl-1-indanamine.** A solution of 0.5 g of N-formyl-1-indanamine in 20 ml of dry ether was added to 0.35 g of lithium aluminum hydride in 10 ml of ether. After 12 hr stirring the excess hydride was hydrolyzed with water and the alumina dissolved by addition of 10% potassium hydroxide. The ether layer was separated and extracted with cold dilute hydrochloric acid. The aqueous phase was evaporated to dryness, giving the crude amine hydrochloride, mp 130°.

The amine was isolated by the decomposition of the hydrochloride in aqueous base and extraction with ether. Removal of solvent gave sufficient material for a nmr spectrum ($CDCl_3$), $\delta$ 1.75–3.05 (4 H, methylene), 2.47 (3 H, N-methyl), 2.88 (1 H, amine), 4.18 (1 H, tertiary as triplet), 7.25 (4 H, aromatic).

**(*R*)-(−)-N-Methyl-1-indanamine.** The optically active formamide, similarly reduced by lithium aluminum hydride, gave a 38% yield of (*R*)-(−)-N-methyl-1-indanamine hydrochloride, mp 136–138°.

The amine was obtained by vpc fractionation using the silicone GE-SF 96 column.

*Anal.* Calcd for $C_{10}H_{13}N$: C, 81.58; H, 8.90. Found: C, 80.64; H, 9.04.

Indanamine, the monomethyl, and the dimethyl compounds were separable by vpc on the silicone GE-SF 96 column at 130°.

The optical purity of the monomethylindanamine was 54% based on that of the starting acid ($[\alpha]^{27}\mathrm{D}$ +23.6°).

RD in isooctane (*c* 0.057, 588–278 m$\mu$; *c* 0.019, 272–238 m$\mu$) showed $[M]^{24}_{588}$ −50.5°, $[M]_{556}$ −68.6°, $[M]_{500}$ −8.34°, $[M]_{294}$ −228°, $[M]_{272}$ +46.2° (peak), $[M]_{270}$ −117° (trough), $[M]_{266}$ −98.0° (peak), $[M]_{244}$ −572°, $[M]_{238}$ −450°; RD in methanol (*c* 0.053, 588–278 m$\mu$; *c* 0.026, 272–238 m$\mu$) showed $[M]^{24}_{588}$ −78.0°, $[M]_{333}$ −74.9°, $[M]_{294}$ 0°, $[M]_{272}$ +555° (peak), $[M]_{269}$ +12.7° (trough), $[M]_{265}$ +53.7° (peak), $[M]_{250}$ −393°, $[M]_{238}$ −218°; RD of amine hydrochloride in methanol (*c* 0.40, 588–333 m$\mu$; *c* 0.020, 333–238 m$\mu$) showed $[M]^{24}_{588}$ −13.1°, $[M]_{410}$ 0°, $[M]_{272}$ +1430° (peak), $[M]_{269}$ +491° (trough), $[M]_{266}$ +804° (peak), $[M]_{253}$ −476°, $[M]_{238}$ +458°.

**N,N-Dimethyl-1-indanamine.** Indanamine (0.80 g) was methylated with 90% formic acid and 27% formaldehyde according to the method used by Icke, Wisegaver, and Alles.[12] The solution was heated to 90–100° for 24 hr. After cooling, 30 ml of 4 *N* hydrochloric acid was added and the solution was evaporated to dryness giving an orange solid which was dissolved in 20 ml of 18 *N* sodium hydroxide. Steam distillation was carried out until the distillate was no longer basic. Extraction of the liberated amine was done with ether and the ether layer was treated with 5 ml of concentrated hydrochloric acid. Evaporation of the acid solution gave a solid which, after vacuum drying, weighed 0.37 g (40%), mp 193–195°.

Dimethyl-1-indanamine was isolated by treatment of the hydrochloride with potassium hydroxide solution, extraction with ether, concentration, followed by final purification *via* vpc using the silicone GE-SF 96 column. The nmr spectrum ($CDCl_3$) showed $\delta$ 1.85–3.05 (4 H, methylene), 2.23 (6 H, N-methyl), 4.30 (1 H, tertiary as triplet), 7.20 (4 H, aromatic).

**(*S*)-(+)-N,N-Dimethyl-1-indanamine.** Using the same procedure as that followed for the preparation of the racemic amine, indanamine (prepared from indancarboxylic acid, $[\alpha]^{27}\mathrm{D}$ −15.2°) was converted to N,N-dimethyl-1-indanamine hydrochloride, mp 196–198°, in 60% yield. The active amine was isolated in the usual fashion by vpc with the silicone GE-SF 96 analysis column.

*Anal.* Calcd for $C_{11}H_{15}N$: C, 81.93; H, 9.38. Found: C, 81.79; H, 9.37.

The optical purity of the dimethylindanamine was 35% based on the starting acid above. Its configuration is opposite that of the other compounds of this series described here; RD in isooctane (*c* 0.066, 588–278 m$\mu$; *c* 0.022, 278–238 m$\mu$) showed $[M]^{24}_{588}$ +45.5°, $[M]_{313}$ +124° (broad), $[M]_{274}$ +16.0° (trough), $[M]_{270}$ +172° (peak), $[M]_{268}$ +39.0° (trough), $[M]_{263}$ +108°, $[M]_{250}$ +82.0°, $[M]_{238}$ +142°; RD in methanol (*c* 0.030) showed $[M]_{556}$ +39.4°, $[M]_{333}$ +87.5°, $[M]_{74}$ −382° (trough), $[M]_{270}$ 0° (peak), $[M]_{268}$ −100° (trough), $[M]_{250}$ +364°, $[M]_{238}$ +138°; RD of amine hydrochloride in methanol (*c* 0.84, 588–357 m$\mu$; *c* 0.020, 333–294 m$\mu$; *c* 0.017; 285–256 m$\mu$) showed $[M]_{588}$ +5.60°, $[M]_{333}$ +13.4°, $[M]_{293}$ 0°, $[M]_{274}$ −800° (trough), $[M]_{270}$ 0° (peak), $[M]_{268}$ −379° (trough), $[M]_{256}$ +750°.

**N,N-Dimethyl-1-indanamine Methiodide.** A solution of 0.20 g of 1-indanamine and 1.0 g of methyl iodide was heated at reflux overnight. A small amount of white methiodide (0.1 g), mp 198–199° (lit.[13] mp 198°), was isolated by filtration and air dried.

**(*R*)-(−)-N,N-Dimethyl-1-indanamine Methiodide.** Indanamine (0.1 g) (prepared from $[\alpha]^{29}\mathrm{D}$ +23.6° acid) was placed in 25 ml of ether and 1.0 g of methyl iodide was added.[13] After 1 day the precipitated solid was filtered off, dissolved in methanol, and reprecipitated with ether. The methiodide (0.1 g) had mp 185–187°. The dispersion curve of the methiodide prepared from the (+)-dimethylindanamine was very similar in shape and general values to that of the methiodide prepared above. The methiodide studied below has an optical purity of 54% based on the starting acid; RD in methanol (*c* 0.030) showed $[M]_{588}$ −46.5°, $[M]_{417}$ −63.5°, $[M]_{313}$ 0°, $[M]_{275}$ +1390° (peak), $[M]_{269}$ −60° (trough), $[M]_{268}$ +436° (peak), $[M]_{250}$ −1000°, $[M]_{244}$ −683°.

## Discussion

Earlier work had indicated that the $^1L_b$ transition[3] (*ca.* 265 m$\mu$) of a number of simple phenyl-substituted hydrocarbons,[29a] alcohols,[29b,c] and acids[29a] did not contribute importantly to their optical activity although Kuhn and Biller[29] did observe first extrema of Cotton effects with derivatives of mandelic and atrolactic acids (see Figures 1–9). More recently, possible first extrema have been reported for a number of aromatic compounds,[30] but the instruments used did not allow any detail to be observed. With modern recording instruments and more powerful light sources better scrutiny of this region of the spectrum has become possible and it is now clear that $^1L_b$ Cotton effects, though often weak, are quite prevalent[4] and often have well-developed fine structure. With our compounds, at least, the $^1L_b$ rotation effects are superimposed on much stronger background rotations which control the sign of rotation in the visible. The background rotation may well be related to the aromatic absorption bands at *ca.* 205 and 185 m$\mu$.

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(29) (a) A. Rothen and P. A. Levene, *J. Chem. Phys.*, 7, 975 (1938); (b) P. A. Levene and A. Rothen, *J. Biol. Chem.*, 127, 237 (1939); (c) W. Kuhn and H. Biller, *Z. Physik. Chem.*, **29B**, 1 (1935).

(30) (a) C. Djerassi, R. Riniker, and B. Riniker, *J. Am. Chem. Soc.*, **78**, 6362 (1956); (b) E. E. Van Tamelen and J. B. Hester, *ibid.*, **81**, 507 (1959); (c) J. L. Mateos and D. J. Cram, *ibid.*, **81**, 2756 (1959); (d) J. M. Bobbitt, U. Weiss, and D. D. Hanessian, *J. Org. Chem.*, **24**, 1582 (1959); (e) V. M. Potapov and A. P. Terent'ev, *J. Gen. Chem. USSR*, **31**, 927 (1961).

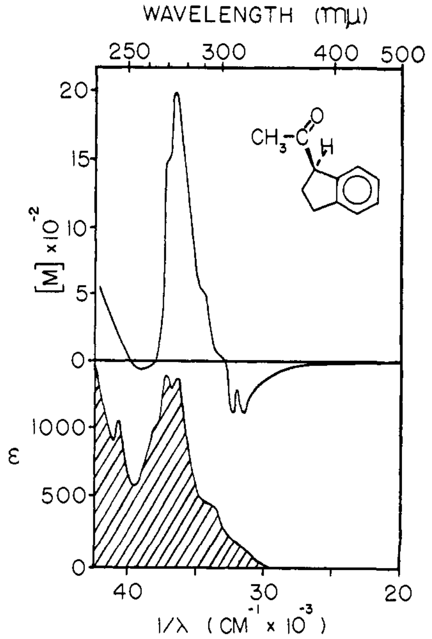

Figure 1. Optical rotatory dispersion (corrected to optical purity) (upper curve) and ultraviolet absorption (lower curve) of (*R*)-(−)-methyl 1-indanyl ketone (both in isooctane).

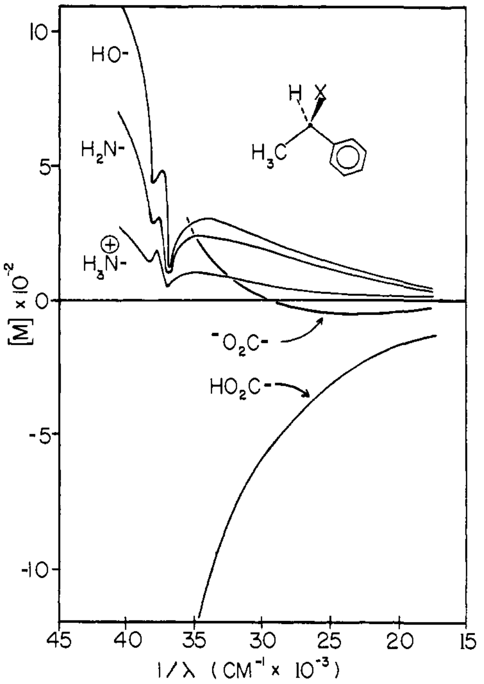

Figure 2. Optical rotatory dispersion of (*R*)-α-phenylethyl compounds: (+)-alcohol (isooctane); (+)-amine (isooctane); (+)-amine hydrochloride (methanol). The curves for the (−) acid (methanol) and its (−) sodium salt (water) were plotted using data for the enantiomers from B. Sjöberg, *Acta Chem. Scand.*, 14, 273 (1960).

The $^1L_b$ Cotton effects are more pronounced in the rigid indan compounds (I) than in the corresponding α-phenethyl compounds (II), where the phenyl group is not "tied down" (compare Figures 2, 5, and 6). Conformational immobilization alone, however, does not suffice, for (*R*)-(−)-1-methylindan (Ih, Figure 4) showed no detectable Cotton effect, while (*R*)-(−)-1-indanol (If, Figure 5), (*R*)-(+)-1-indanylcarbinol (Ig, Figure 4), and (*R*)-(−)-1-indanamine (Ic, Figure 6) and its derivatives (Figures 7, 8, and 9) all showed pronounced Cotton effects. The sodium salt of (*R*)-(+)-1-indancarboxylic acid (Ib, Figure 3) showed no detectable Cotton effect although the acid (Ia, Figure 3) did.

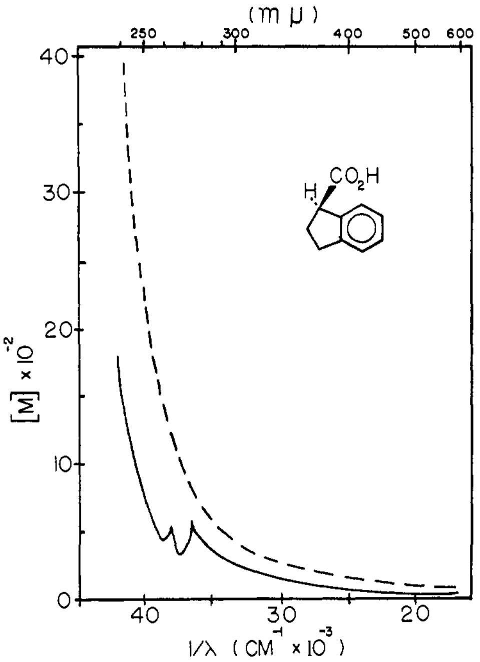

Figure 3. Optical rotatory dispersion (corrected to optical purity) of (*R*)-(+)-1-indancarboxylic acid (Ia) in methanol (———) and of its sodium salt (Ib) in water (- - - -).

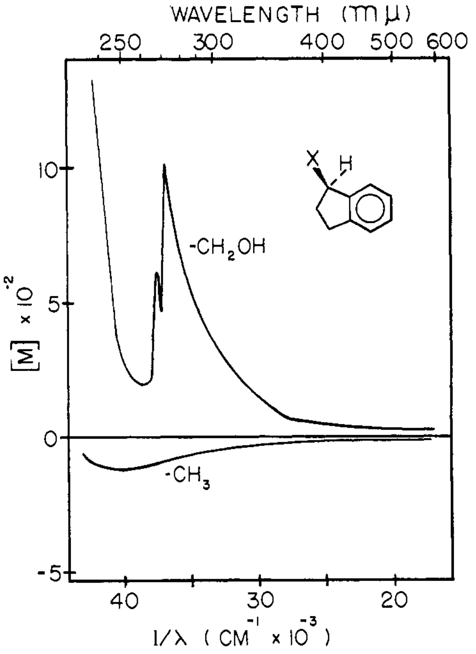

Figure 4. Optical rotatory dispersion (corrected to optical purity) of (*R*)-(+)-1-indanylcarbinol (upper curve) and (*R*)-(−)-1-methylindan (lower curve), both in isooctane.

We suggest that dissymmetric hydrogen bonding to the aromatic nucleus[31] may be one way in which strong $^1L_b$ Cotton effects can be produced. Infrared bands

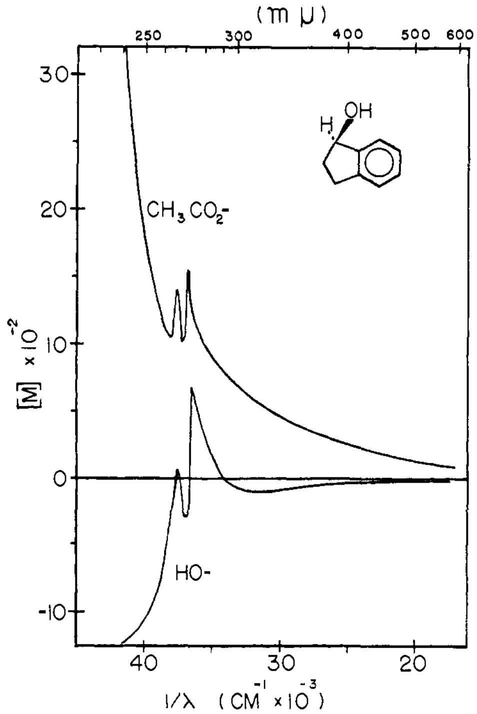

Figure 5. Optical rotatory dispersion (corrected to optical purity) of (*R*)-(−)-1-indanol in isooctane (lower curve) and of (*R*)-(+)-1-indanyl acetate in isooctane (upper curve).

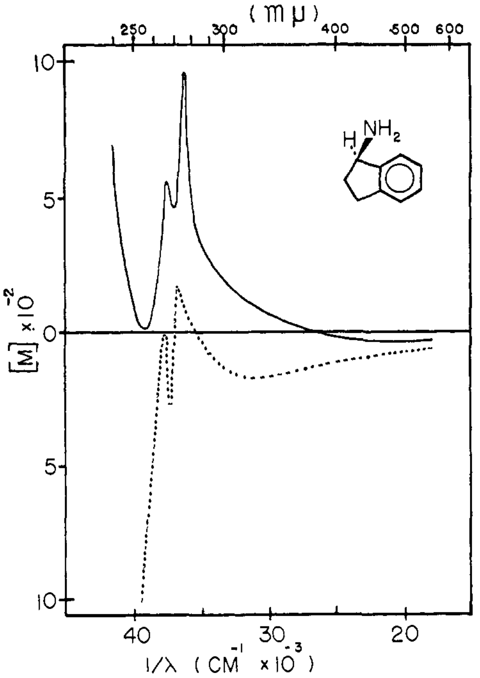

Figure 6. Optical rotatory dispersion (corrected to optical purity) for (*R*)-(−)-1-indanamine (Ic) in isooctane (. . . .) and for its hydrochloride (Id) in methanol (———).

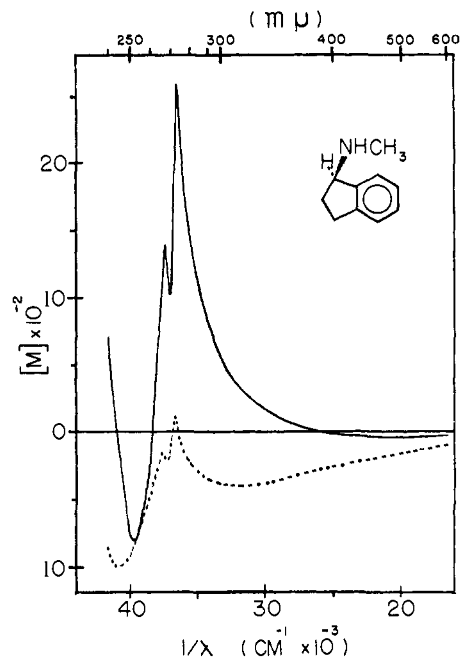

Figure 7. Optical rotatory dispersion (corrected to optical purity) of (*R*)-(−)-N-methyl-1-indanamine in isooctane (. . . .) and of its hydrochloride in methanol (———).

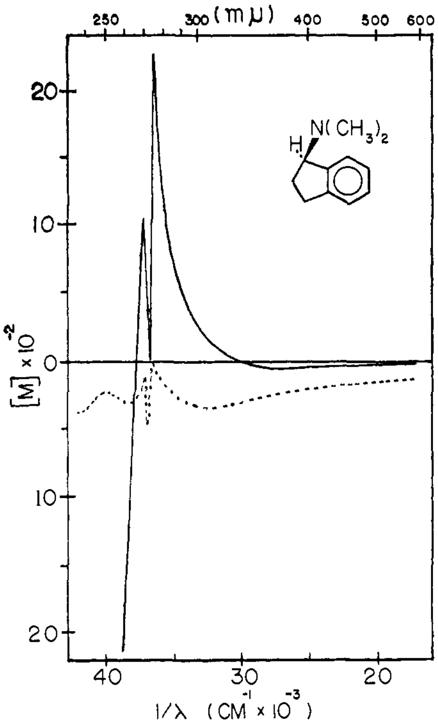

Figure 8. Optical rotatory dispersion (corrected to optical purity) for (*R*)-(−)-N,N-dimethyl-1-indanamine in isooctane (. . . .) and for its hydrochloride in methanol (———). Actual measurements made on the *S* isomers.

indicating internal hydrogen bonding[31] were observed with highly dilute carbon tetrachloride solutions of 1-indanol (free OH, 3620 cm$^{-1}$; bonded, 3605 cm$^{-1}$; roughly equal strength) and 1-indanylcarbinol (free OH, 3638 cm$^{-1}$; bonded, 3605 cm$^{-1}$; ratio *ca.* 2:1). The latter case is closely comparable to that of β-phenylethanol for which we find: free OH, 3638 cm$^{-1}$; bonded, 3605 cm$^{-1}$; ratio 1.5:1, in agreement

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(31) (a) A. M. Buswell, W. H. Rodebush, and R. M. Whitney, *J. Am. Chem. Soc.*, 69, 770 (1947); (b) D. S. Trifan, J. L. Weinmann, and L. P. Kuhn, *ibid.*, 79, 6566 (1957); (c) P. von R. Schleyer, C. Wintner, D. S. Trifan, and R. Backsai, *Tetrahedron Letters*, 14, 1 (1959); (d) H. Kwart and R. T. Keen, *J. Am. Chem. Soc.*, 81, 943 (1959); (e) M. T. Davies, D. F. Dobson, D. F. Hayman, G. B. Jackman, M. G. Lester, V. Petrow, O. Stevenson, and A. A. Webb, *Tetrahedron*, 18, 751 (1962); (f) E. Galantay, *ibid.*, 19, 319 (1963).

with earlier work.[31b-d] For $\alpha$-phenylethanol we find a single band, at 3616 cm$^{-1}$, in agreement with earlier work,[31b,c] but our result with indanol suggests that the region near 3618 cm$^{-1}$ may be the normal position for the absorption peak of an unbonded benzylic hydroxy group. In that case it becomes possible that there is no monomolecular hydrogen bonding to the aromatic nucleus in $\alpha$-phenylethanol. Such hydrogen bonding does, however, remain possible in dimeric species; perhaps the small $^1L_b$ Cotton effects arise in this way. The large increase in the size of the Cotton effect which accompanies conversion of the indanamines to their hydrochlorides (Figures 6, 7, and 8) might be attributable to hydrogen bonding but it seems clear, from the example of the quaternary salt (Ie, Figure 9), that positive charge is also very important. The fact that sterically crowded phenyl terpenes and steroids[32] give $^1L_b$ Cotton effects indicates that simple crowding may also have to be taken into account in some of these cases.

One of our more significant findings is that configurationally related indans (I) and $\alpha$-phenethyl compounds (II) have ORD curves of essentially mirror-image shape,[33] with both the background rotations (which control the [M]D values) and the $^1L_b$ Cotton effects being of opposite sign. It seems clear that factors other than simple configuration at an asymmetric center ("atomic asymmetry")[34] are important in *both* series. In particular, we suggest that conformation III, in which the methyl group is coplanar with the ring, would have rotatory properties analogous to those of the corresponding indan (I) and that conformation IV, in which the group X is coplanar with the ring, would have rotatory properties analogous to those of (*S*)-(+)-1-methylindan (V). Since conformations III and IV correspond to energy maxima for rotation of the phenyl group they will not contribute appreciably to the optical rotatory properties of II. But if there were no conformational energy maxima the phenyl group would give no $^1L_b$ Cotton effect since it would, on a time average, assume all possible conformations and so "see" its environment as being effectively symmetrical (at least with respect to pairwise interactions[35]). Accordingly, the net dispersion curve of II should have a shape that is essentially the mirror image of the sum of the dispersion curves of the missing conformations (III and IV)[36] or of their bicyclic analogs, I and V. Since methylindan (V) shows no major rotation anomalies in this region it follows, on this basis, that I and II should have essentially mirror image dispersion curves *because* they have the same configuration at the asymmetric center. This argument suggests that the "atomic asymmetry rule"[34] may not reflect "atomic asymmetry" at all in the phenyl series, but, rather, the effects of a rotationally important interaction of a heteroatom with the phenyl group.[32,37]

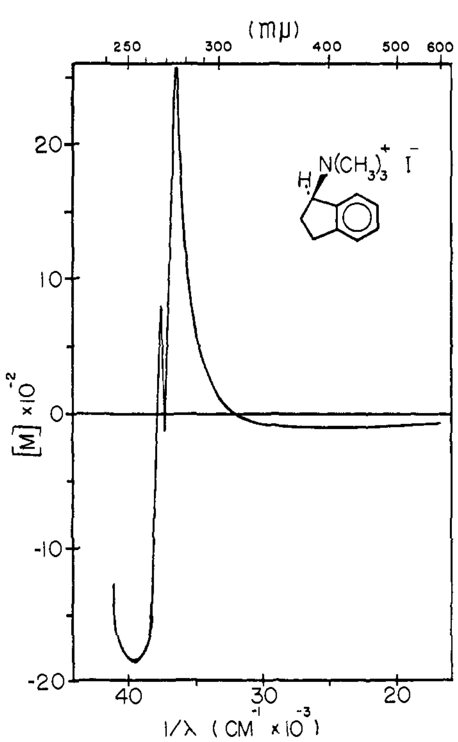
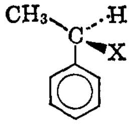
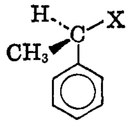


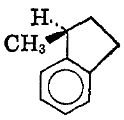
Figure 9. Optical rotatory dispersion (corrected to optical purity) for (*R*)-(−)-N,N,N-trimethyl-1-indanylammonium iodide (Ie) in methanol.



III



IV



V

It will be noted that the argument presented above depends on the assumption that the rotationally important electric dipole transition moment of the benzene chromophore has the same geometric relationship to the asymmetric center in series I and II. This assumption would probably be invalid if the direction of the moment were controlled *solely* by the atoms directly attached to the nucleus since in that case the $^1L_b$ moment of II would be directed as in VI while that of I would be directed as in VII.[38] In the present cases, however, a large Cotton effect appears to be associated with the presence of a group capable of direct perturbation of the $\pi$ electron cloud of the ring by hydrogen bonding or by electrostatic or steric effects. It does not seem unreasonable to consider that such a group would be prepotent and could, in effect, wash out the relatively minor effects due to saturated carbon atoms in the plane of the ring. If so, strong $^1L_b$ Cotton effects *attributable to this kind of interaction with the $\pi$ electrons of the ring* should follow a simple sector rule, keyed to

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[32] J. H. Brewster, W. E. Braden, and A. S. Kurasiewicz, unpublished.

[33] This conclusion rests on Fredga's assignment of configuration to (*R*)-(+)-1-indancarboxylic acid (Ia).[7] Evidence that this is correct is provided by the ORD curve of (−)-methyl 1-indanyl ketone, prepared from the (+)-acid by use of methyllithium. This shows a negative Cotton effect centered at about 286 mμ and giving evidence of homoconjugation. Only those conformations in which the phenyl group is in a negative octant of the keto group have the correct geometry for overlap of the aromatic $\pi$ orbitals with both the $n_p$ and $\pi^*$ orbitals of the keto group. See A. Moscowitz, K. Mislow, M. A. W. Glass, and C. Djerassi, *J. Am. Chem. Soc.*, **84**, 1945 (1962); S. MacKenzie, S. F. Marsocci, and H. C. Lampe, *J. Org. Chem.*, **30**, 3328 (1965).

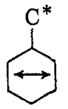
[34] J. H. Brewster, *J. Am. Chem. Soc.*, **81**, 5475 (1959).

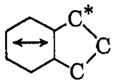
[35] W. Kauzmann, F. B. Clough, and I. Tobias, *Tetrahedron*, **13**, 57 (1961).

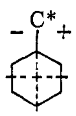
[36] Due allowance should be made for intensity as a function of concentration and for the probability that II would show a plain dispersion curve over the accessible portion of the spectrum even if it had no conformational energy maxima.

[37] J. H. Brewster, *Tetrahedron Letters*, 20, 23 (1959).

[38] See P. E. Stevenson, *J. Chem. Educ.*, **41**, 234 (1964) for a brief, but clear, review.


VI


VII


VIII

the axes of polarizability of a mono-substituted benzene. Our data are consistent with the octant rule portrayed in VIII where plus and minus indicate the sign of the $^1L_b$ Cotton effect due to a strongly interacting group above the plane of the ring. Effects of this nature do not seem to have been considered in detail in the theoretical treatments of the phenyl chromophore.[4f,39] We do not feel qualified, however, to pursue the theoretical analysis beyond this point and hope that it will be taken up by someone else.

(39) D. J. Caldwell and H. Eyring, *Ann. Rev. Phys. Chem.*, **15**, 281 (1964).

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# The Protonation and Indicator Behavior of Some Ionic Azobenzenes in Aqueous Sulfuric Acid

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*Contribution from the Research Laboratories, Eastman Kodak Company, Rochester, New York 14650.* *Received December 2, 1965*

**Abstract:** The effect of ionic solubilizing groups on the indicator behavior of weak organic bases has been examined. The concentration ratios, $C_{BH^+}/C_B$, and apparent basicities, $pK'_{BH^+}$, of a number of anionic and zwitterionic *para*-substituted phenylazobenzenes and 2-(*para*-substituted phenylazo)-1-naphthols were measured in 1–80 wt % sulfuric acid. Several monoanionic and all the zwitterionic bases behaved as $H_0$ indicators, whereas other monoanionic and a dianionic base showed small deviations from this scale. Poorer parallelism was obtained with other acidity function indicators. Apparent $pK'_{BH^+}$ values, based on the $H_0$ scale, gave excellent correlation with $\sigma_p$ constants for the phenylazonaphthols and with $\sigma^+$ constants in the case of the phenylazobenzenes, with the exception of the *p*-NMe$_2$ derivative. The unprotonated phenylazonaphthols exist almost exclusively as the tautomeric phenylhydrazones in water, whereas the protonated species exist as the resonance-stabilized azonium ions. Monoprotonation of methyl orange gives a mixture of the azonium ion and ammonium ion in which the former is predominant. Monoprotonation of the *p*-NMe$_2$ derivative in the azonaphthol series gives the ammonium ion almost exclusively. Possible reasons for adherence to the $H_0$ scale and the significance of the apparent $pK'_{BH^+}$ values are discussed.

We were interested in examining the effect of an ionic solubilizing substituent on the activity coefficient ratios of weak organic bases in which the basic center is nonionic. The establishment and evaluation of acidity function scales have to date been largely confined to weak bases where the unprotonated species is a nonionic molecule. The Hammett $H_0$ scale, as modified by Jorgenson and Hartter,[1] is based on nitrated primary anilines. It has been established that other bases that differ little in structure from the nitrated primary anilines[2] show different indicator properties, and generate their own acidity function scales that vary somewhat from the $H_0$ scale. Other weak bases whose indicator behavior has been examined include tertiary anilines,[2] aliphatic ethers,[3] amides,[4,5] azobenzenes,[6] azulenes,[7] arylolefins,[8] indoles,[9] phenols[10] and phenolic ethers,[10,11] pyrroles,[12] and uracils.[13] In each case, the indicator properties did not paralle those of the nitrated anilines used to fix the $H_0$ scale, as indicated by slopes, d log $(C_{BH^+}/C_B)/dH_0$, that deviated from unity. Somewhat less work has been done on evaluating acidity function scales for ionic indicators. Michaelis and Granick utilized the successive protonation of 3-aminothiazine and of 3,9-diaminothiazine to define part of a scale in aqueous sulfuric acid that was based on the mono- and dications.[14] Boyd has defined a scale ($H_-$) based on cyanocarbon acids that are anionic in their basic form.[15] With the latter indicators, the charged center and the basic center are the same. DeLigny and co-workers have measured the p$K_a$'s of 4-aminophenylazobenzene-4′-sulfonic acid and several of its N-substituted derivatives in methanol–water mixtures (p$K'$) and found that the differences, p$K'$ − p$K$, vary with solvent composition in quite different ways from the differences for uncharged indicators.[16] From this they conclude that $H_0$ is not a useful measure of acidity for these indicators in aqueous methanol.

We have investigated the indicator behavior of a series of structurally similar ionic azo compounds in aqueous sulfuric acid to determine the extent to which they conform to existing acidity function scales.

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