Optically Active Amines. 25.[1] Circular Dichroism of 1-Substituted Indans

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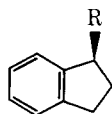**and Fu-Ming Chen**[2b,3]

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Abstract: Cyclization of (*S*)-β-phenylbutyric acid to (*S*)-3-methyl-1-indanone and Clemmensen reduction of the latter gave (*S*)-1-methylindan. Since this isomer is levorotatory in benzene, the earlier assignment of the *S* configuration to the dextrorotatory isomer is corrected. The circular dichroism spectra of (*S*)-1-methylindan and other 1-substituted indans having the same relative configuration show, except for potassium (*S*)-1-indanylcarboxylate, negative Cotton effects near 270 nm associated with the ^1L_b transition of the benzene chromophore. When the substituent is an alkyl, hydroxyl, or amino group, these Cotton effects cannot be explained by the coupled oscillator mechanism, possibly owing to the dominance of a negative one-electron contribution to the rotational strength. When a carboxylate, carboxyl, carbonyl, or acyloxy group is or is part of the C(1) substituent, the ^1L_b transition of the benzene chromophore may couple with a $\pi \rightarrow \pi^*$ transition of the substituent and may cause the coupled oscillator contribution to overshadow that of the one-electron mechanism. Only in the case of potassium (*S*)-1-indanylcarboxylate does this coupling give rise to positive Cotton effects for the ^1L_b transition. The observed Cotton effect near 215 nm for (*S*)-1-methylindan and the other 1-substituted indans, except for (*S*)-1-aminoindan, is negative and is due to either the ^1L_a transition of the benzene chromophore or exciton splitting of the ^1L_a transition and a transition near 215 nm of the C(1) substituent. The positive Cotton effect shown by (*S*)-1-aminoindan may be due to the effect of the $n \rightarrow \sigma^*$ transition at about 210 nm of the amino group. Protonation of the amino group eliminates the $n \rightarrow \sigma^*$ transition and results in a reversal of the sign of the Cotton effect.

In a previous paper,[1] an analysis was made concerning the factors which cause the sign of the ^1L_b Cotton effects of chiral para-substituted norephedrines to be opposite from that of their unsubstituted analogues. It was shown that the reversal in sign is due to a change in sign of the rotatory contribution of the chiral center adjacent to the benzene chromophore. This contribution can be subdivided into static (one-electron) as well as dynamic (coupled oscillator) mechanisms.[4] In the unsubstituted compounds, the one-electron mechanism is dominant. On para substitution, the transition moment becomes larger, and the oppositely signed contribution of the coupled oscillator mechanism may overshadow that of the one-electron mechanism.

In the course of this work, our attention was drawn to a similar analysis by Allen and Schnepp[5] of the mechanism by which the ^1L_b Cotton effects of (*S*)-1-methylindan [(*S*)-1] (Chart I) are generated. In this work, a theoretical calculation, using (*S*)-1 with a planar five-membered ring and 5.1×10^{-19} esu cm for the benzene ^1L_b transition moment, gave positive values for both the one-electron ($+4.1 \times 10^{-41}$ cgs units) and coupled oscillator ($+2.4 \times 10^{-41}$ cgs units) contributions to the Cotton effect of the ^1L_b band origin. The validity of the calculation was supported by the experimental observation of

positive Cotton effects for the ^1L_b transition in the gas-phase circular dichroism (CD) of the dextrorotatory (sodium D line with benzene as the solvent) enantiomer of 1-methylindan. Based on earlier work by Brewster and Buta,[6] this enantiomer was assigned the *S* configuration.[5]

Further, the ^1L_b rotational strength for (*S*)-1-methylindan [(*S*)-1] was calculated by Dickerson and Richardson[7] using the CNDO/S method for the planar (I) and two nonplanar conformations [II with the methyl group quasi-axial (a) and C(2) below (−) the benzene ring plane, and III with the methyl
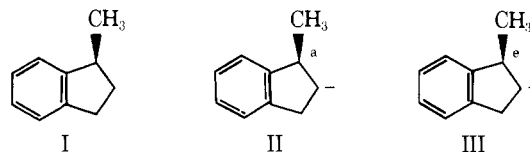
group quasi-equatorial (e) and C(2) above (+) the benzene ring plane] of the cyclopentene ring. Conformers I and II were calculated to give a positive contribution to the ^1L_b Cotton effects and conformer III a negative contribution. It was also calculated that conformer II is more stable than conformer III by about 0.01 eV. On the assumption of an equilibrium mixture of the three conformers, the sign of the ^1L_b Cotton effects for (*S*)-1 was predicted by Dickerson and Richardson[7] to be positive, in agreement with the experimental observation of Allen and Schnepp.[5]

There are indications in the report of Allen and Schnepp,[5] however, that the configurational assignment of the 1-methylindan used in the CD measurements was incorrect. As outlined, the enantiomer of 1 was prepared from an enantiomer of β-phenylbutyric acid (2) (Scheme I), the latter isolated by fractional crystallization and subsequent hydrolysis of the diastereomeric esters prepared from (±)-2 and *l*-menthol. As reported earlier,[8] the strongly levorotatory *l*-menthyl ester of 2 [[α]^{20}D −76.26° (benzene)] on hydrolysis yields the levorotatory isomer of 2 [[α]^{20}D −57.23° (benzene)]. This acid, however, has been unequivocally assigned the *R* configuration by its conversion to (*S*)-hydratropic acid[9] [(*S*)-4] (Scheme II) which in turn has been related to (*S*)-α-phenylethylamine[10] [(*S*)-5], a compound of certain absolute configuration estab-

Chart I

(*S*)-1, R = CH₃	(*S*)-18, R = NH₂CH₃Cl
(*S*)-6, R = OH	(*S*)-19, R = NH(CH₃)₂Cl
(*S*)-7, R = NH₂	(*S*)-20, R = N(CH₃)₃I
(*S*)-8, R = NH₃Cl	(*S*)-21, R = CO₂K
(*S*)-9, R = CH₂OH	(*S*)-22, R = CO₂H
(*R*)-10, R = C(CH₃)₃	(*S*)-23, R = COCH₃
(*S*)-11, R = C(CH₃)₂CH₂OH	(*S*)-24, R = CH₂CO₂K
(*S*)-12, R = C(CH₃)₂CH₂NH₂	(*S*)-25, R = C(CH₃)₂CO₂K
(*S*)-13, R = C(CH₃)₂CH₂NH₃Cl	(*S*)-26, R = CH₂CO₂H
(*S*)-14, R = C(CH₃)₂CH₂Br	(*S*)-27, R = C(CH₃)₂CO₂H
(*S*)-15, R = CF₃	(*S*)-28, R = CH₂COCH₃
(*S*)-16, R = NHCH₃	(*S*)-29, R = OCOCH₃
(*S*)-17, R = N(CH₃)₂	(*S*)-30, R = CH₂OCOCH₃

Table I. Spectral Data for 1-Substituted Indans

compd	solvent	^1L_b band origin maxima		215-nm band maximum	
		λ, nm (ϵ^a)	λ, nm ($[\theta]^b$)	λ, nm (ϵ^a)	λ, nm ($[\theta]^b$)
(S)-1	gas phase[c]	271.3 (760)	270.9 (−430)	217.5 (910)	217.5 (−1300)
	methanol	273 (1300)	274 (−1100)		222 (−6000)
	hexane	273 (1800)	272 (−780)		
(S)-6	methanol[d,e]	272 (920)	271 (−1490)	214 (4720)	219 (−2440)
(S)-7	cycohexane[f]	273 (804)[g]	273–274 (−200)	210 (7800)	210–213 (+27 800)
(S)-8	methanol[h]	272 (1000)	271 (−1300)		negative[i]
(R)-10	methanol[d,j]	272 (1290)	274 (−4050)	212 (5940)	224 (−6870)
(S)-21	methanol[d,e]	274 (1190)	276 (+715)	215 (5370)	228 (−14 200)
(S)-22	methanol[d,e]	273 (850)	273 (−147)	213 (5090)	227 (−5700)

[a] Molar absorptivity. [b] Molecular ellipticity. [c] Data adapted from that in ref 5 for (R)-1. [d] Data from ref 15. [e] Enantiomer used. [f] Data from ref 16. [g] Shoulder at 280 nm (ϵ 294) which is assumed not to be in the 0←0 transition of the ^1L_b band. [h] Data from ref 14. [i] Assigned on the basis of a peak, $[\phi]_{219}$ +3800°, in the ORD spectrum of (R)-8 in methanol reported in ref 15. [j] See note 24.

Scheme I

Scheme II
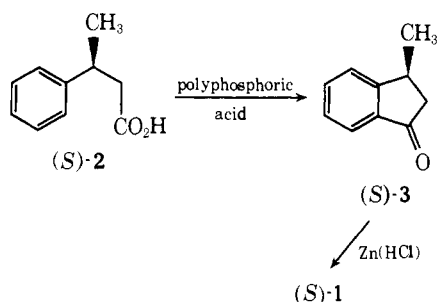
lished both by the X-ray method[11] and chemical correlation.[12]

The *l*-menthyl ester of **2** used by Allen and Schnepp[5] was strongly levorotatory [[α]$_D$ −79.6° (state not reported)] and presumably gave (R)-**2** on hydrolysis. Subsequent synthetic operations must then lead to (R)-**1**.

We deemed it essential to establish unequivocally the rotatory powers of the enantiomers of 1-methylindan (**1**) because of their importance as a gauge to test the correctness of theoretical calculations of rotational strength.[5,7,13] Further, we wished to examine the CD of an enantiomer of **1** in various solvents and to compare these spectra with those of other 1-substituted indans[6,14-16] (Chart I) as a continuation of our interest[1,14] and that of others[5,7,13-17] in the chiroptical properties of the benzene chromophore.

Results and Discussion

Configuration of 1-Methylindan (1). As outlined earlier,[18,19] resolution of (±)-β-phenylbutyric acid [(±)-**2**] by fractional crystallization of the (S)-α-phenylethylamine salts from ethanol-water gave (S)-**2**. Cyclization of the acid chloride of (S)-**2** at room temperature in benzene using aluminum chloride as catalyst[19] gave (S)-3-methyl-1-indanone [(S)-**3**]. Clemmensen reduction[20] of (S)-**3** afforded (S)-**1**.

Since the magnitude of the rotatory power of (S)-**3** was essentially the same as that reported earlier using polyphosphoric acid[21] or hydrogen fluoride[22] as reaction medium and catalyst for the cyclization of one or the other enantiomers of **2**, only an insignificant amount of racemization occurred during cyclization using aluminum chloride in benzene, in contrast to the complete racemization of optically active 2-phenylbutane when treated with aluminum chloride at 0 °C without solvent.[18]

As reported earlier there is a substantial solvent dependence on the rotatory power of both (S)-**1**[23] and (S)-**3**.[21] The former was optically inactive in hexane and in methanol and only showed easily measurable levorotation without solvent and in benzene. The latter is dextrorotatory without solvent[19,22] and in acetone and levorotatory in benzene.[21] Since (S)-**1** is levorotatory in benzene, the enantiomer used by Allen and
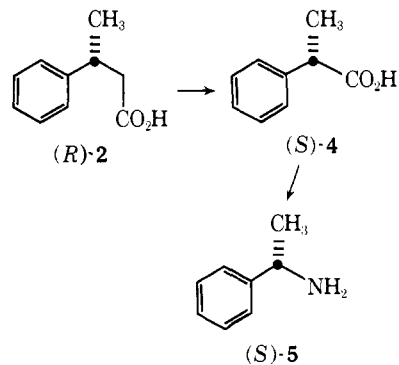
Schnepp[5] in their CD measurements had the R configuration.

Circular Dichroism. The isotropic ultraviolet absorption (UV) and CD spectra for (S)-1-methylindan are given in the Experimental Section, and the UV and CD maxima for the ^1L_b band origin and for the transition near 215 nm for (S)-**1** are compared with similar data for a few other chiral 1-indans in Table I. The UV and CD and/or optical rotatory dispersion (ORD) spectra of the other 1-substituted indans in Chart I[24] have also been reported,[6,14-16] and in general show three to four UV maxima and corresponding Cotton effects from about 255-275 nm which arise by transitions to totally symmetric vibrational modes of the ^1L_b excited state of benzene. Except for those of (S)-**21**, these Cotton effects for the configuration depicted in Chart I are negative. The Cotton effect at about 215 nm is that of the ^1L_a transition of the benzene chromophore if the substituent at C(1) does not have a transition in this spectral region. Although the sign of this short-wavelength Cotton effect cannot be deduced for a number of the 1-substituted indans in Chart I (**16–20, 23,** and **29**) from either their ORD or CD spectrum, the observed Cotton effect at about 215 nm for all of the compounds with the configuration shown in Chart I is negative, except for (S)-**7** which shows a positive Cotton effect at about 212 nm (Table I).
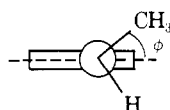
^1L_b **Cotton Effects.** The ^1L_b Cotton effects are assumed to arise by a combination of static (one-electron) as well as dynamic (coupled oscillator) mechanisms. Using the planar conformation for (S)-1-methylindan [(S)-**1**], the coupled oscillator contribution was calculated by Allen and Schnepp[5] to be positive, opposite in sign to the observed Cotton effects.

To investigate the effect of nonplanar conformations of the cyclopentene moiety of (S)-**1** on the dynamic contribution to the rotational strength, a coupled oscillator calculation[25] was made with point dipoles approximated to be at the center of the benzene chromophore and at the center of the C(1)-methyl group bond, the latter assumed to be the sole dissymmetric

Table II. Six Lowest Energy Excited States of Indan[a]

| | | | | transition | |
| | | | | moment | |
symmetry	type	wavelength, nm	oscillator strength	electric (μ), D	magnetic (m), μ_B
$2A_1$	$\pi \to \pi^*$	275.1	0.007	0.627 (z)	
$1B_2$	$\pi \to \pi^*$	218.2	0.045	1.441 (y)	0.007 (x)
$1A_2$	$\sigma \to \pi^*$	197.0	0.000		0.587 (z)
$1B_1$	$\sigma \to \pi^*$	194.9	0.001	0.152 (x)	0.087 (y)
$3A_1$	$\pi \to \pi^*$	190.3	1.167	6.869 (z)	
$2B_2$	$\pi \to \pi^*$	189.0	1.061	6.527 (y)	0.117 (x)

[a] Indan is taken to have C_{2v} symmetry. The z axis is the C_2 axis and the yz plane is the plane of the carbon skeleton.

Table III. Rotational Strengths Due to the Coupled Oscillator Contribution[a]

| | rotational strength, cgs units $\times 10^{40}$, for dihedral angle, ϕ | | | | | | | |
transition	10°	20°	30°	40°	50°	60°[b]	70°	80°
$1A_1 \to 2A_1$ (B_{2u} or ^1L_b)	+0.093	+0.182	+0.263	+0.331	+0.385	+0.422	+0.443	+0.446
$1A_1 \to 1B_2$ (B_{1u} or ^1L_a)	−0.121	−0.280	−0.510	−0.836	−1.26	−1.78	−2.37	−2.97
$1A_1 \to 3A_1$ (E_{1uA} or ^1B_b)	+23.7	+46.2	+66.6	+84.0	+97.6	+107	+112	+113
$1A_1 \to 2B_2$ (E_{1uB} or ^1B_a)	−3.50	−8.12	−14.8	−24.3	−36.7	−51.7	−68.7	−86.3

[a] Transition moments and frequencies of the chromophore are those of Table II. The C(1)–methyl group bond transition moment and frequency are 3.75 D and 2.3×10^{15} Hz, respectively. [b] Corresponds to a planar cyclopentene ring.

perturber of the chromophore. The transition moments and frequencies used were calculated for indan using the CNDO/S method,[26,27] modified to include the magnetic transition moments.[28] The results are shown in Table II for the six lowest energy excited states. The coupled oscillator contributions were calculated for the four lowest energy, electrically allowed transitions and are shown in Table III for various dihedral angles (ϕ) of the methyl group with respect to the benzene ring plane. As can be seen in Table III, the dynamic contribution to the rotational strength of the ^1L_b transition is always positive for positive dihedral angles of 10–80° with a steady increase in magnitude as the angle becomes larger.

To demonstrate that this result is not an artifact of the point dipole approximation of the chromophore transition moment, another calculation was made in which this moment was resolved along bonds and then a bond by bond coupling[25] was employed to obtain the rotational strength. The coupled oscillator contribution was again found to be positive for positive dihedral angles of 10–80°. It thus follows that the coupled oscillator contribution to the ^1L_b Cotton effects of (S)-1 and those of the other 1-substituted indans not containing an additional chromophoric group (6–20) in CHART I is positive. The observed negative ^1L_b Cotton effects for these 1-substituted indans may then be due to the dominance of a negative one-electron contribution to the rotational strength.

An earlier theoretical calculation by Caldwell and Eyring,[29] however, does not support a negative contribution by the one-electron mechanism. This calculation, which considered the mixing in of a Rydberg $3d_{z^2}$ orbital with the valence π system, gives a positive one-electron contribution to the rotational strength of (S)-1. That this result is in disagreement with the present experimental observation of negative ^1L_b Cotton effects for (S)-1 may be due to the neglect of nearby $\sigma \to \pi^*$ and $\pi \to \sigma^*$ transitions of A_2 symmetry. These transitions may have magnetic transition moments along the indan C_2 axis which can mix with the electric moment of the ^1L_b transition and by dissymmetric perturbation produce the observed Cotton effects. This suggestion is supported by the results of our CNDO/S calculation for indan (Table II). As seen in Table

II, a $\sigma \to \pi^*$ transition of A_2 symmetry with a substantial magnetic moment is found at 197 nm. The CNDO/S calculation by Dickerson and Richardson[7] for the rotational strength of the planar (I) and two nonplanar (II and III) conformers of (S)-1 gives for each conformer a $\sigma \to \pi^*$ transition near 197 nm of considerable rotational strength. The gas-phase absorption spectrum of (R)-1[5] shows two small shoulders at 196.7 and 193.6 nm with corresponding negative and positive maxima at 198.1 and 194.3 nm in the CD spectrum. These two transitions may thus be assigned to the $1A_2$ (197.0 nm) and $1B_1$ (194.9 nm) $\sigma \to \pi^*$ transitions, respectively, in the present calculation. The sizable magnetic moment associated with the $1A_2$ transition as well as its close proximity to the ^1L_b band may thus be responsible for the one-electron contribution to the ^1L_b Cotton effects in (S)-1 being negative and overshadowing the positive coupled oscillator contribution. The same may be true for the other 1-substituted indans in Chart I (6–20) which do not incorporate as part of the C(1) substituent a group with a strong electrically allowed transition close to the ^1L_b transition.

When a carboxylate, carboxyl, carbonyl, or acyloxy group is or is part of the C(1) substituent there is now present a $\pi \to \pi^*$ transition which may couple strongly with the ^1L_b transition of the benzene chromophore and may cause the coupled oscillator contribution to overshadow that of the one-electron mechanism. This is seen in the CD spectrum of potassium (S)-1-indanylcarboxylate [(S)-21] which shows positive Cotton effects for the ^1L_b transition.

The electric transition moments of the two energetically identical, local carbonyl $\pi \to \pi^*$ transitions[30] of the carboxylate group below 210 nm will form components parallel with and perpendicular to the group's symmetry axis. The perpendicular component is deemed ineffective because of rotational averaging about the carboxylate group attachment bond. Thus a positive coupled oscillator contribution to the Cotton effects of the ^1L_b transition of (S)-21 can be predicted from the chirality of the carboxylate group attachment bond and the ^1L_b transition moment, using the point dipole approximation for the latter at the center of the benzene ring.

For (S)-1-indanylcarboxylic acid [(S)-22], the coupled oscillator contribution is less easily analyzed since a symmetry axis for the group is not present. The presence of the carboxyl group, however, does not result in the sign of the ^1L_b Cotton effects being different from that of (S)-1-methylindan [(S)-1]. The same is true for (S)-1-acetylindan [(S)-23] and the other 1-substituted indans in Chart I, in which a carboxylate (24 and 25), carboxyl (26 and 27), carbonyl (28), or acetyloxy (29 and 30) group is or is part of the C(1) substituent. The coupling of the associated $\pi \rightarrow \pi^*$ transition may be such that it either augments the negative one-electron contribution or makes only an insignificant positive contribution to the rotational strength, and the observed ^1L_b Cotton effects are negative.

That the ^1L_b rotational strength of (S)-1-methylindan [(S)-1] calculated directly by the CNDO/S method by Dickerson and Richardson[7] is positive for the planar conformation (I) and for the nonplanar conformation with the methyl group quasi-axial (II) and negative for the conformation with the methyl group quasi-equatorial (III) can be rationalized in terms of the static (one-electron) and dynamic (coupled oscillator) contributions to the rotational strength. In this connection, Snatzke, Kajtar, and Snatzke[17] proposed a sector rule for 1-substituted indans based on the nodal and symmetry planes of indan (IV). This rule can be regarded as one-electron


IV
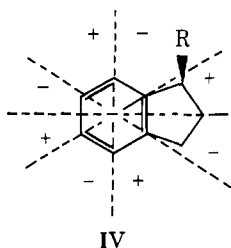
in origin. As can be seen in IV, the smaller the dihedral angle ϕ in (S)-1 (cf. Table III), the closer is the perturbing methyl group to the center of a negative sector. As the dihedral angle increases, the negative one-electron contribution becomes smaller and eventually crosses a sector boundary and becomes positive. The positive coupled oscillator contribution starts from a small value but steadily increases as the dihedral angle increases (Table III). Thus for the conformer with the methyl group in the quasi-equatorial orientation (III), the one-electron mechanism dominates, and for the planar conformation (I) and that with the quasi-axial methyl group (II), the coupled oscillator mechanism is the more important. The observed negative ^1L_b Cotton effects then suggest a preferred nonplanar conformer with the methyl group quasi-equatorial (III), in disagreement with the configurational energy calculation of Dickerson and Richardson[7] noted above. A nonplanar conformation of (S)-1, however, is supported by the Raman spectrum of indan which favors C_s rather than C_{2v} symmetry.[31]

215-nm Band. The Cotton effect at about 215 nm is clearly due to the ^1L_a benzene transition if the perturber does not have a transition in this spectral region. The shorter wavelength and the larger transition moment of the ^1L_a band as compared to those of the ^1L_b band suggest the dominance of the coupled oscillator mechanism for the former. Indeed the experimental observations with (S)-1-methylindan [(S)-1] agree with the calculation shown in Table III for the coupled oscillator mechanism. Similar to those for the ^1L_b transition, the calculated results disagree with those of Dickerson and Richardson[7] for conformers I and II but agree for conformer III.

When the C(1) substituent gives rise to an electrically allowed transition at about 210 nm, exciton splitting of this transition with the ^1L_a benzene transition occurs, as evidenced by a shift of the CD maximum to a longer wavelength than the

UV maximum (cf. (S)-21 and (S)-22 in Table I). The sign of the longer wavelength maximum of the CD couplet will, however, be negative regardless of whether the longer wavelength transition making up the couplet is associated with the perturber transition or the ^1L_a benzene transition. As predicted by the coupled oscillator mechanism, the observed Cotton effects near 215 nm for the 1-substituted indans in Chart I (1, 6, 8–15, 21, 22, 24, 28), except that for (S)-1-aminoindan [(S)-7] (Table I), are all negative. For (S)-7, the positive CD maximum may be due to the effect of the n→σ* (or 3s) transition at about 210 nm of the amino group.[32] Protonation of the amino group [(S)-8] eliminates the n→σ* transition and results in a reversal of the sign of the Cotton effect. This latter observation is similar to that made by Gottarelli and Samori[33] in which the positive CD maximum at about 210 nm for (S)-α-phenylethylamine [(S)-5] and some of its para-substituted derivatives [(S)-31] in cyclohexane changes sign in 10% hydrochloric acid.
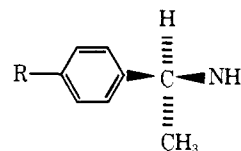
(S)-31, R = CH$_3$, OCH$_3$, Cl, or Br

Since the sign of the Cotton effect near 215 nm for (S)-16 and (S)-17 could not be assigned from either their ORD or CD spectra, the influence of N-alkyl substitution on the Cotton effect displayed by (S)-1-aminoindan could not be assessed. Only the ORD spectrum of (R)-23 has been reported[6] and the ^1L_a Cotton effect was not observed.

Experimental Section

The melting point was taken in an open capillary tube and is corrected. The boiling points are also corrected. Optical rotations were measured at the sodium D line using a visual polarimeter and a 1-dm sample tube. The isotropic ultraviolet absorption (UV) spectra were obtained with a Cary Model 14 spectrophotometer with the normal variable slit and matched 1-cm cells. The circular dichroism (CD) spectra were measured with a Cary Model 60 spectropolarimeter with a CD Model 6001 accessory at 25–28 °C using a 1-cm cell. The slit was programmed for a spectral band width of 1.5 nm, and cutoff was indicated when the dynode voltage reached 400 V. The parameters used in the CNDO/S calculation were those reported.[27] The geometry of indan used in the calculation follows: C$_{Ph}$-C bond length, 1.50 Å; C-C bond length, 1.54 Å; C$_{Ph}$-C$_{Ph}$-C bond angle, 112.5°; C$_{Ph}$-C-C bond angle, 101.8°; and the aromatic ring geometry, that of benzene.

(S)-β-Phenylbutyric Acid [(S)-2]. Resolution of (±)-2 was accomplished using (S)-α-phenylethylamine, $[\alpha]^{25}_D$ −39° (neat). Five recrystallizations from ethanol–water gave a pure salt (44%): mp 145–147 °C; $[\alpha]^{26}_D$ +8.5° (c 1.6, CH$_3$OH) (lit.[19] mp 144.5–146 °C). Decomposition of this salt gave (S)-2 (77%): bp 103–110 °C (0.3 mm); $[\alpha]^{26}_D$ +55° (c 1.5, benzene) [lit.[22] $[\alpha]^{25}_{589}$ −57.6° (c 2.7, benzene) for (R)-2].

(S)-3-Methyl-1-indanone [(S)-3]. Using a procedure previously outlined,[19] (S)-2 was converted to its acid chloride with thionyl chloride in benzene. Addition of aluminum chloride to a benzene solution of the acid chloride, boiling of the mixture for 1.5 h, and isolation of the product in the usual way gave (S)-3 (60%): bp 103–105 °C (4.9 mm); α^{26}_D +3.8° (neat); $[\alpha]^{26}_D$ +17° (c 2.8, acetone); $[\alpha]^{26}_D$ −2° (c 2.2, benzene) [lit. bp 112–113.5 °C (9 mm) and $[\alpha]^{25}_D$ +3.8° (neat) using aluminum chloride in benzene as cyclization medium,[19] $[\alpha]^{20}_D$ +16° (c 2, acetone) and $[\alpha]^{20}_D$ −1.4° (c 1, benzene) using polyphosphoric acid as cyclization medium,[21] and α^{25}_{589} −4.08° (neat, 1 dm) for (R)-3 using liquid hydrogen fluoride as cyclization medium[22]].

(S)-1-Methylindan [(S)-1]. Employing a well-known procedure, method 1 in ref 20 for the Clemmensen reduction of β-(p-toluyl)-propionic acid, (S)-3 was converted to (S)-1 (41%): bp 108–110 °C (70 mm); n^{25}_D 1.5241; α^{26}_D −11.9° (neat); $[\alpha]^{26}_D$ −11° (c 2.1, benzene); $[\alpha]^{26}_D$ ±0° (c 2.1, hexane); $[\alpha]^{26}_D$ ±0° (c 2.6, CH$_3$OH)

[lit. bp 189.5 °C (739.2 mm) and n^{25}D 1.5241 for (±)-1[34] and $[\alpha]_D$ +14° (benzene) for (R)-1[5]]; UV max (CH$_3$OH) 273 (ϵ 1300), 266 (1200), 260 (780), 254 nm (460) (sh); (hexane) 273 (ϵ 1800), 267 (1400), 260 (1000), 255 nm (710) (sh); CD (CH$_3$OH) (c 0.0149) $[\theta]_{350}$ ±0, $[\theta]_{290}$ ±0, $[\theta]_{274}$ −1100, $[\theta]_{271}$ −370, $[\theta]_{267}$ −1000, $[\theta]_{261}$ −710 (sh), $[\theta]_{243}$ ±0, $[\theta]_{232}$ ±0, $[\theta]_{222}$ −6000, $[\theta]_{219}$ −4400; (hexane) (c 0.0126) $[\theta]_{350}$ ±0, $[\theta]_{277}$ ±0, $[\theta]_{272}$ −780, $[\theta]_{267}$ −550, $[\theta]_{265}$ −1000, $[\theta]_{250}$ ±0.

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The Properties of Clusters in the Gas Phase. 2. Ammonia about Metal Ions

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Abstract: Thermochemical properties of cluster ions, involving Li$^+$ and Na$^+$ solvated by ammonia, were measured using high-pressure mass spectrometry. Investigation of the equilibria over a wide range of temperature for the reactions M$^+$(NH$_3$)$_n$ + NH$_3$ ⇌ M$^+$(NH$_3$)$_{n+1}$ enabled a determination of both the enthalpies and entropies of clustering. With M = Li$^+$, the enthalpies are found to be 33.1, 21.0, 16.5, 11.1, and 9.3 kcal/mol for n = 1, 2, 3, 4, and 5, respectively. For M = Na$^+$, the enthalpies, with n ranging from 0 to 5, are 29.1, 22.9, 17.1, 14.7, 10.7, and 9.7 kcal/mol, respectively. In contrast to our recent results for K$^+$ and Rb$^+$, data for both Li$^+$ and Na$^+$ show a significant decrease in bond energy for the attachment of the fifth ammonia molecule to a cluster containing four ligands. These findings suggest the existence of a solvation shell of four ligands in the case of both Li$^+$ and Na$^+$. Comparison of the bond energies of the monoligand clusters shows that the ammonia molecule bonds more strongly than H$_2$O for all alkali metal ions. This is consistent with a simple molecular orbital model which is based on the difference in ionization potentials of the metal and ligand. Quantitative account of the relative trends for the difference in the binding of NH$_3$ and H$_2$O to Li$^+$, Na$^+$, K$^+$, and Rb$^+$ is obtained from calculations made with the extended Hückel method.

Introduction

Investigation of the formation, properties, and structure of small clusters in the gas phase represents a very active area of current research. Results of studies, both involving molecules clustered about ions as well as neutral molecules clustered among themselves, are of interest for several reasons. In particular, there is a growing realization that studies of clusters in the gas phase provide requisite data for elucidating the nature and extent of ion-solvent and solute-solvent interactions which are important in solution chemistry.[1,2] The results give detailed information on forces operating in individual complexes, but without interferences arising from the presence of the bulk solvent.

Data on the formation and stability of clusters are also needed in advancing the theory of phase transitions and the attendant phenomenon of nucleation.[3] In addition, the results of such studies are expected to contribute to an understanding of the development of surfaces[4] and the nature of forces involved in the formation of disperse systems[5] such as micelles, colloids, and aerosols.

Research is currently underway in our laboratory on both neutral and ion cluster reactions. The development of high-pressure mass spectrometric methods, which are applicable for measuring the thermodynamic properties of individual ion clusters, has prompted us to devote considerable attention to studies of the interactions of ions with molecules. Since the interaction potentials between ions and polar molecules are well known, ion clusters are particularly amenable to theoretical calculation and the experimental data find immediate value for comparison with theory.

In order to establish the role of chemical bonding in stabi-