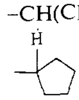
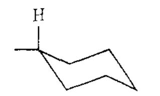
Table I. Angular Independent Shift Contributions $\vartheta_0(\beta)$, Rotational Barriers V_2, and Equilibrium Conformations θ_0 of complexes **1a**-**j** from −60 to +130°

Compound	$-CHR^1R^2$	$\vartheta_0(\beta)$, ppm	V_2, kcal/mol	θ_0, deg
1a	$-CH_3$	15.5	0	60 ± 2
1b	$-CH_2CH_3$	17 ± 3	2.5 ± 0.3	60 ± 2
1c	$-CH_2CH_2CH_3$	14.5 ± 4	3.7 ± 0.5	60 ± 2
1d	$-CH_2C_6H_5$	13.5 ± 2	3.2 ± 0.3	60 ± 2
1e	$-CH_2CH_2C_6H_5$	20 ± 2	3.2 ± 0.3	60 ± 2
1f	$-CH(CH_3)_2$	15.5 ± 5	4.1 ± 0.3	68 ± 3
1g		12.5 ± 4	2.3 ± 0.2	69 ± 3
1h		11 ± 5	3.7 ± 0.2	72 ± 2
1i	$-CH(CH_3)C_2H_5$	13.5 ± 3	4.2 ± 0.2	76 ± 2
1j	$-CH(C_2H_5)_2$	13.5 ± 2	4.5 ± 0.3	83 ± 3

2p orbital, eq 2.[6] Formula **2** illustrates the structural situation, looking from C^α toward C^c and the nickel. The expec-

$$\vartheta(\beta) = \vartheta_0(\beta) + \vartheta_2(\beta)\langle\cos^2\theta\rangle \quad (2)$$

$$\langle\cos^2\theta\rangle = \int\cos^2\theta\cdot e^{-V(\theta)/RT}d\theta \Big/ \int e^{-V(\theta)/RT}d\theta \quad (3)$$

$$V(\theta) = V_2\sin^2(\theta - \theta_0) \quad (4)$$

tation value $\langle\cos^2\theta\rangle$ may be computed classically by eq 3 yielding the same result as the quantum mechanical procedure.[7] Assuming the $\sin^2$ potential energy function[8] of eq 4, we compute a theoretical temperature dependence which is shown as the heavy trace through the β-shifts in Figure 1. The parameters used in these calculations have been collected in Table I; additionally, $\vartheta_2(\beta)$ in eq 2 equals −200 (±20) ppm for all complexes. The specified error limits indicate which variations of one parameter may be canceled by suitable changes of the others.

One of the two conformations of lowest energy for **1a**–**e** is depicted in formula **2** with each $C^\alpha H^\beta$ bond at $\theta_0 = 60°$. Rotations by ±90° will produce the energy maxima with C^β in the chelate plane. This picture agrees perfectly with an *ab initio* calculation[10] for ethylbenzene which should be a good model for **1b**. The computed[10] barrier of 2.2 kcal/mol compares well with **1b** in Table I. Conformation **2** is also supported by dibenzyl[11] as a model for **1e** as well as by esr[12] and vibration spectroscopy.[13] The vanishing barrier to methyl rotation[14] in **1a** shows up as a totally temperature-invariant shift $\vartheta(\beta)$.

The parameters for *sec*-alkyl groups in **1f**–**j** were derived by assuming two barriers at θ = 0 or 180°, *i.e.*, when the single β-hydrogen eclipses the 2p orbital. The equilibrium angles θ_0 in Table I, resulting from a slight modification of eq 4, compare well with esr results[12b] on isopropylbenzene (64°), cyclopentylbenzene (66°), and cyclohexylbenzene (74°). The barrier of 3.9 kcal/mol computed for cyclohexylbenzene[15] agrees with that of **1h**. It is also evident from Table I that cyclopentyl[16] and ethyl[17] groups rotate much easier than isopropyl[16,17] and cyclohexyl.[16]

Our ϑ_0/ϑ_2 ratio of −0.08 is to be compared with theoretical ratios of −0.03[6b,d,e] or +0.03[6c] or +0.055.[6f] A recent experimental estimation[18] was between −0.02 and −0.06.

Dipolar shifts[2] will not contribute to the overwhelming part (ϑ_2) of our β-shifts if the rotation axis $C^\alpha C^c$ of the β-hydrogens coincides with the magnetic axis of **1**.

Acknowledgment. Support by the Stiftung Volkswagenwerk and the Deutsche Forschungsgemeinschaft is gratefully acknowledged.

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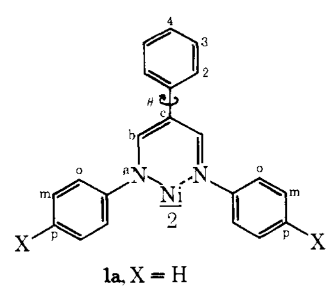
Conformational Analysis by Spin Transmission into Rotating and Rigid Phenyl Groups

Sir:

The Curie law is generally valid for nickel complexes of the chelate type **1**.[1] Therefore, the previously[1] defined re-



1a, X = H
b, X = C_2H_5
c, X = n-C_3H_7
d, X = OC_2H_5

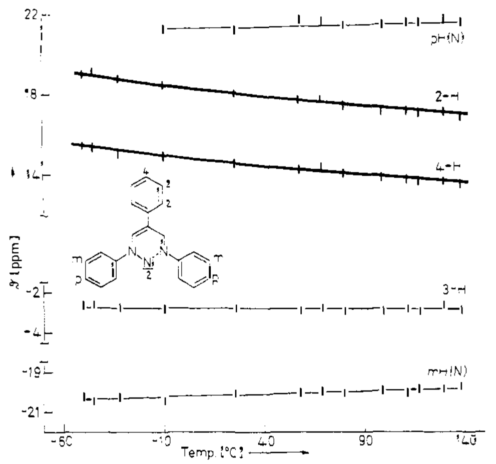


Figure 1. Isotropic reduced shifts ϑ of **1a** as a function of temperature.

Table I. Parameters of Angular Dependent (ϑ_2) and Independent (ϑ_0) Shift Contributions from -50 to $+140°$

Compound	ϑ_0 (2-H) ($\pm$1 ppm)	ϑ_2 (2-H) ($\pm$3 ppm)	ϑ_0 (4-H) ($\pm$0.5 ppm)	ϑ_2 (4-H) ($\pm$2 ppm)
1a	4.65	18.0	1.95	17.0
1b	5.0	18.0	2.35	17.0
1c	5.25	18.0	2.65	17.0
1d	5.55	17.5	2.55	17.0

duced ^{1}H nmr shifts[2] ϑ_i of **1a–d** should be independent of the temperature. Figure 1 exemplifies this expectation for the meta and para protons of the *anilino* groups in **1a**. Simultaneously, ϑ (2-H) and ϑ (4-H) of the *phenyl* group attached to C^c in **1** decrease with increasing temperature. We ascribe this apparent deviation from the Curie law to thermally excited phenyl rotation.

Transmission of positive spin density (as measured by ϑ_i) from the 2p orbital at C^c of the chelate ring[1] into the phenyl group is a function of the interplanar angle θ and presumably described by eq 1.[3] We approximate the rotational potential energy function by eq 2 with a minimum at θ_0 and a barrier, V_2, in the perpendicular conformation (no conjugation).

$$\vartheta = \vartheta_0 + \vartheta_2\langle\cos^2\theta\rangle \qquad (1)$$

$$V(\theta) = V_2 \sin^2\left(\frac{\theta - \theta_0}{90^0 - \theta_0}90^0\right) \qquad (2)$$

Theoretical shifts ϑ were computed as previously described[1] and drawn as the heavy traces through the experimental 2- and 4-hydrogen shifts in Figure 1. Table I shows the parameters of eq 1 which produce such traces in combination with $V_2 = 1.3$ ($\pm$0.2) kcal/mol and $\theta_0 = 5$ ($\pm 5°$). The specified uncertainties indicate which variations of one parameter may be balanced by suitable modifications of the others.

Our ϑ_0/ϑ_2 pattern and the weak angular dependence of ϑ(3-H) (compare Figure 1) agree reasonably well with INDO calculations[4] on the twisting benzyl radical. Since the frequent assumption[5] of a very small ϑ_0 in eq 1 is not borne out here, we searched for independent support as follows. Lack of temperature dependence of any shift ϑ in **2** and **3** is consistent with perpendicularly locked phenyl groups ($\cos^2 90° = 0$). Accordingly, ϑ (2-H) and ϑ (4-H) in **2**/**3** have dropped rather closely to ϑ_0 although some spin density might survive in the π-system.[6] This shift pattern deviates from the relative coupling constants of most radicals with reportedly twisted aryl groups.[4b,c,7]

On the other hand, the shifts (slightly extrapolated

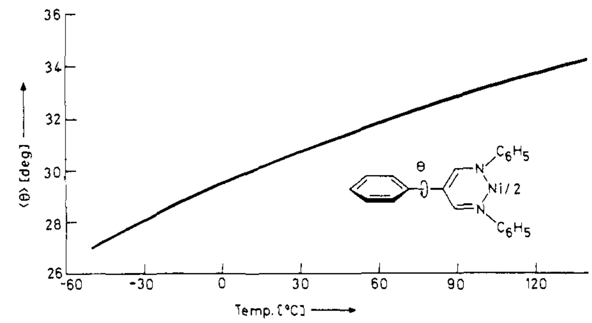
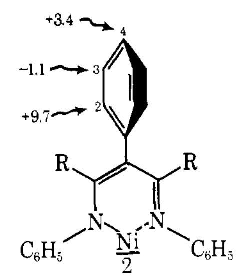
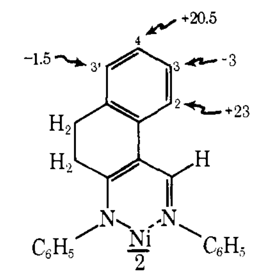


Figure 2. Apparent interplanar angles $\langle\theta\rangle$ (degrees) for **1a** as a function of temperature.



2, R = CH_3
3, R = C_2H_5



4

toward 0°K) denoted in formula **4** for the almost coplanar[8] ($\cos^2\theta = 1$) phenyl group agree perfectly with $\vartheta_0 + \vartheta_2$ from Table I.

Theoretical calculations[9] on biphenyl as a model for **1** locate a highest barrier (experimentally unknown)[10] of 2–4 kcal/mol either at $\theta = 90°$ [5a–e] or at $\theta = 0°$.[5a,f,g] Computed equilibrium angles θ_0 of about 40° contrast with experimental estimates[11] from 0 to 45°. However, eq 1 and 2 imply that angles θ_0 around 45° would cause temperature *in*dependent shifts for **1**. *Apparent* interplanar angles $\langle\theta\rangle$ may be calculated by eq 1 from the experimental shifts ϑ of **1a** together with ϑ_0 and ϑ_2 from Table I. Figure 2 demonstrates this powerful method of conformational analysis. If **1a** is indeed comparable to biphenyl, our $\langle\theta\rangle$ values might indicate thermally averaged angles in some literature estimates.

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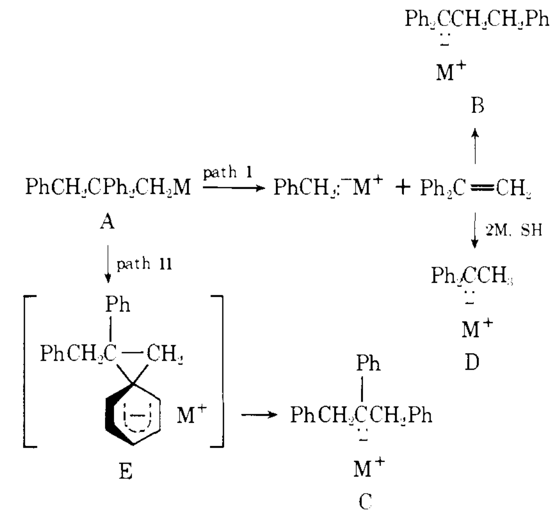
Carbanions. XV. Tight and Loose Ion Pairs in Rearrangements of Organoalkali Compounds[1]

Sir:

Whereas 2,2,3-triphenylpropyllithium (A), prepared from reaction of 1-chloro-2,2,3-triphenylpropane with lithium at −65 to −75°, has been reported[2] to rearrange in tetrahydrofuran (THF) at 0° with at least 98% 1,2-migration of benzyl, we now find that reaction of the same chloride with cesium in THF at 65° gives 96% 1,2-migration of phenyl rather than benzyl. In order better to understand the phenomena responsible for such diverse migratory aptitudes, the rearrangement has been studied under widely variable conditions as reported in Table I. Previous work[3] has indicated (see Scheme I) that benzyl migration proceeds by elimination of benzyl anion and readdition of this anion to 1,1-diphenylethene to give B (path I) while aryl migration proceeds intramolecularly *via* a spiro anion to C (path II). In the present work 1,1-diphenylethyl anion (D) has been identified; indeed D is a major product under strongly reducing conditions with solutions[4] of alkali metals (*e.g.*, potassium plus 18-crown-6 in THF). It is reasonable to suppose that this anion results from reduction of intermediate 1,1-diphenylethylene. The appearance of D along with benzyl anion[5] constitutes additional evidence for the occurrence of path I.

Scheme I



Examination of Table I reveals that 2,2,3-triphenylpropyllithium does not rearrange at an appreciable rate upon standing in the THF at −75°, even upon addition of 18-crown-6 ether;[6] however, sodium *tert*-butoxide or better potassium and cesium *tert*-butoxides are effective catalysts, with the product being notably dependent upon the cation present. For a related rearrangement, lithium *tert*-butoxide, unlike potassium or cesium *tert*-butoxides was an ineffective catalyst.[7] These pronounced cation effects suggest that the cation plays an important role in determining the fate of the anion and imply that the cation must be geometrically close to the anion during the rearrangement process. This could be understood, for example, if the rearrangement catalyzed by cesium *tert*-butoxide took place in the corresponding organocesium compound; therefore, the following metathetical reaction appears to occur under our conditions

$$PhCH_2CPh_2CH_2Li + MO\text{-}t\text{-}Bu \longrightarrow PhCH_2CPhCH_2M + LiO\text{-}t\text{-}Bu \quad (1)$$

Additional evidence (see Table I) for this metathesis comes from the similar ratio (equal within likely experimental errors) of products of path I to path II observed for the reaction of cesium metal with the chloride at −75° as compared to the reaction of cesium *tert*-butoxide with the organolithium compound at the same temperature.

Table I. Rearrangements of 2,2,3-Triphenylpropyl Alkali Metal Compounds

Conditions	Temp, °C	Products,[a] rel mol % A	B	C	D
$PhCH_2CPh_2CH_2Li$, 7 hr, THF	−75	100	0	0	0
$PhCH_2CPh_2CH_2Li$ + 2(18-crown-6), 3.3 hr, THF	−75	100	0	0	0
$PhCH_2CPh_2CH_2Li$, 30 min, THF	0	0	100	0	0
$PhCH_2CPh_2CH_2Li$, 3 hr, Et_2O	+35	0	0	100	0
$PhCH_2CPh_2CH_2Li$ + 2NaO-*t*-Bu, 30 min, THF	−75	33	58	0	9
$PhCH_2CPh_2CH_2Li$ + 2KO-*t*-Bu, 30 min, THF	−75	0	63	37	0
$PhCH_2CPh_2CH_2Li$ + 2CsO-*t*-Bu, 30 min, THF	−75	0	25	72	3
$PhCH_2CPh_2CH_2Li$ + 2KO-*t*-Bu + 2(18-crown-6), 30 min, THF	−75	0	100	0	0
$PhCH_2CPh_2CH_2Li$ + 2CsO-*t*-Bu + 2(18-crown-6), 30 min, THF	−75	20[b]	77	0	3
$PhCH_2CPh_2CH_2Cl$, K, THF	+65	0	10	90	0
$PhCH_2CPh_2CH_2Cl$, Cs, THF	+65	0	2	96	2
$PhCH_2CPh_2CH_2Cl$, Cs,[c] THF	−75	0	5	67	28
$PhCH_2CPh_2CH_2Cl$ + 2(18-crown-6), excess K, THF	−75		2	0	98
$PhCH_2CPh_2CH_2Cl$ + 2(18-crown-6), excess Cs,[c] THF	−75	0	0	<8	>92[d]

[a] Yields are based only on acidic products from carbonation; the entry "0" % means that none was detected by the nmr and glpc techniques used and therefore less than 1 or 2% was present. [b] The reaction is apparently retarded by precipitation of a cesium *tert*-butoxide complex with the 18-crown-6. [c] The organoalkali product was treated with excess mercury to lower activity of cesium (destruction of radical anions) prior to carbonation. [d] The measured ratio of **C**:**D** was 8:92 in this run; however, since the ratio of Cs:18-crown-6 was 1.15:1 and the adventitious presence of an impurity caused most of the cesium to react, it is thought that the yield of C would have been reduced if an excess of 18-crown-6 over cesium had been present.