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Substituent-Induced Chemical Shifts along the C=N Bond of Schiff Bases

Rudolf Knorr*, Kathrin Ferchland, Johann Mehlstäubl, Petra Böhrer, Thi Phung Hoang, and David S. Stephenson

Institut für Organische Chemie der Universität München,
Karlstraße 23, W-8000 München 2, F.R.G.

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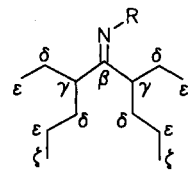
Sterically congested *N*-(1,1,3,3-tetraalkyl-2-indanylidene)-amines **8**–**11**, *N*-(cyclopentylidene)anilines **13**–**17**, and two of their salts are described, together with a short synthesis of 2-imino-1,1,3,3-tetramethylindan (**5**). Some of these imines show rapid (*E,Z*) equilibration. Positively and negatively charged nitrogen functions (in **6** and **7**) cause opposite ^1H- and ^{13}C-NMR chemical shift effects along the C=N bond. Chemical shifts are almost equally affected by the lone electron pair and by the imino N–H bond. Substituent-induced chemical shifts (SCS) have been assigned for all *syn* and *anti* positions with respect to methyl, phenyl, and 2,6-dimethylphenyl groups at the imino nitrogen atom. The structurally well-defined, rigid imines recommend themselves as new models for the calibration of theoretical approaches to *syn/anti*-differentiating SCS.

Substituent-induced chemical shifts[2] (SCS) are defined as the differences of corresponding NMR chemical shifts, $\Delta\delta_k = \delta_k(R) - \delta_k(R = H)$, between an R-substituted compound and the parent (unsubstituted) substance. For NMR-active nuclei (k) at the point of attachment (α) of the perturbing substituent or at the next position (β), such increments are empirically well-known, and are important in a first constitutional confirmation of new compounds. Long-range SCS (k positions γ, δ, ε, etc.), if stereochemically distinctive, can be very useful for the assignment of stereoisomers; but they frequently pose severe problems because of their small size and the possibility of orientation-dependent sign changes of $\Delta\delta$, often without straightforward relations to the number of intervening bonds. The conformational problem may be simplified by studying SCS in unsaturated compounds like **1**, and the present paper intends to contribute evidence from two series of structurally rather rigid, sterically congested imines, **5**, **8**–**11** and **12**–**17**, with little or no conformational ambiguity. Their precise structures are easily predicted by force-field calculation or even by inspection (and confirmed in a case related to **16** by X-ray analysis[3]). Most of their ^{13}C- and some ^1H-NMR assignments are rigorous, including those of one of the parent (NH) compounds, as based on a variety of methods like nuclear Overhauser effects, (*E,Z*) equilibration[4], coupling relations, methylation shifts, and deuteration with resultant isotopic shifts. Although the ^{13}C-NMR spectra of many imines are documented[5], their assignment have not always proved conclusive[4], and only the differential (*syn* vs. *anti*) shielding could be reported[4,6] rather than SCS values because reliable data for the parent compounds (NH) were not available.

A. Syntheses and Properties of some Sterically Congested Imines

The *N*-unsubstituted imine **5** has been made[7] by treatment of the oxime **3** with nitrosyl chloride and subsequent ammonolysis of the resulting nitrimine **4**. Nitrosyl chloride is unstable in THF, however, and despite successful repetition we found this procedure so inconvenient that we synthesized **5** by direct reduction of **3** as follows. The oxime **3** is not a sensitive compound as claimed but crystallizes so readily under our conditions that large and even very impure batches of the ketone **2**[8] can be used for its preparation. Since **3** could not be hydrogenated catalytically and since it reacts with $LiAlH_4$ in refluxing THF by overreduction, we adapted the reduction[9] by $TiCl_3$, succeeding in 89% conversion of **3** into **5** while keeping the concomitant acidic hydrolysis of **5** to **2** below 3%. Purification of **5** became easy after a careful investigation of its stability. The previous failure to obtain a correct analysis and melting point is probably due to the conspicuous basicity of **5** rather than to a putative[7] sensitivity: **5** is less basic than triethylamine but more basic than pyridine in $CDCl_3$ solution; the stable hydrochloride **6** precipitates from **5** with concentrated hydrochloric acid and regenerates pure **5** by deprotonation.



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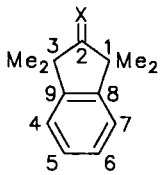

2 - 7

	X
2	O
3	N-OH
4	$N\text{-}NO_2$
5	NH
6	NH_2^+ Cl^-
7	N^- Li^+

Titration of a THF solution of **5** with methyllithium yields the thermally stable lithium imide **7**; its constitution follows from a series of derivatives[10]. Proton exchange between **5** and **7** in coexistence is slow on the NMR-time scale at −64°C (^{13}C NMR).

The *N*-substituted imines **8**–**11** were prepared from the corresponding ketones by modification of the $TiCl_4$ method[11] before the productive synthesis of **5** had been

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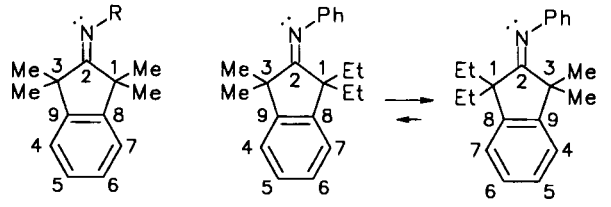
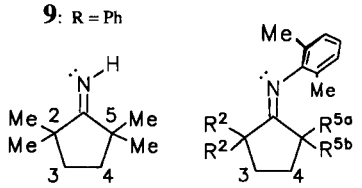
invented. Purification by extraction into and from aqueous acid took advantage of the distinct kinetic stability of **8**–**11** against hydrolysis. Other attempts to synthesize **9** failed: The ketone **2** did not react in boiling xylene with the di-Grignard derivative of aniline[12]; its hydrazone[8] or tosylhydrazone could not be converted into the diazo compound (for intended[13] addition to nitroso benzene) under our conditions without methyl migration to give 1,1,2,3-tetramethylindene, which also forms by treatment of **2** with $TiCl_4$ uncomplexed by an amine. Methylation of 2-(phenylamino)-indene[14] failed to give **9**[15] because of rapid condensation by uncharged or anionic bases.



5: R = H
8: R = Me
9: R = Ph

10 (*Z*) **11** (*E*)



12

13 - 17

	R^2	R^{5a}	R^{5b}
13	H	H	H
14	Me	H	H
15	Me	Me	H
16	Me	Me	Me
17	Et	Me	Me

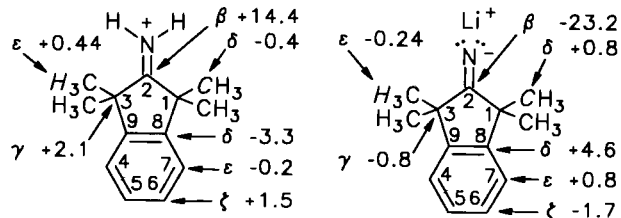
The known multistep syntheses[7,16] of 2,2,5,5-tetramethylcyclopentanimine (**12**) are cumbersome and thus do not recommend **12** as a general starting material for exchange with primary amines. We therefore prepared the anils **15** and **16** from **13** by a methylation procedure which will be published separately. However, the 2,2-dimethyl derivative **14** could be synthesized directly from the ketone **20** and was then transformed into **17** by double ethylation.

B. Lone Electron-Pair and Electric Field Effects

NMR spectra of the imine **5** at ambient temperature are deceptively simple in CCl_4, $CDCl_3$, and diethyl ether, showing apparent C_{2v} symmetry. For example, equivalence of all four methyl groups is due to chemical shift averaging by (*E,Z*) diastereotopomerization of nuclei in the corresponding *syn* and *anti* positions with respect to NH. At −50°C and below the symmetry is reduced to C_s, depending on the solvent. However, the same decoalesced spectra (Table 1) can be observed already at room temperature when a trace of 2 N NaOH is added to the NMR solution. Much weaker concentrations of this base, and also of sodium carbonate solution or of triethylamine, are not sufficient to produce this effect which is completely reversible. Hence, it must be caused by the rapid equilibrium with a trace of the symmetrical cation of **6**, whereas the suggested[17] bimolecular exchange mechanism by dimers[18] may be confined to sterically less hindered imines. For comparison, *syn/anti* splitting by the NH group was reported without assignment for the imines of 2-methylbutyrophenone (^{1}H NMR below −30°C in pentane)[17] and di-*tert*-butyl ketone (^{1}H NMR at −60°C)[19] but could not be observed for 2-methyl- (at −27°C)[20] or 2,4,6-triisopropylbenzophenone imine (at −100°C)[21].

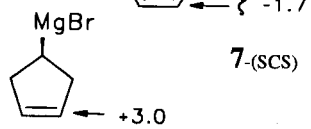
A comparison of the averaged and decoalesced spectra of **5** in Table 1 identifies only the pairs of nuclei in corresponding (*E,Z*) positions. The detailed *syn/anti* assignments became possible by finding an Overhauser enhancement for the NH proton on irradiation of the *syn*-methyl protons resonating at higher field. NOESY experiments in CCl_4/NaOH confirmed this but proved unable to differentiate the aromatic CH functions because the C_6H_4 proton system is strongly coupled even at 400 MHz. However, C-1,3 and C-8,9 could be assigned unequivocally by selective $\{^1H\}$ decoupling ($^2J_{CH}$ and $^3J_{CH}$) of the two methyl groups. The NH proton was found coupled to C-2 by $^2J_{CH}$ = 9.9, to C-1 by $^3J_{CH}$ = 7.5, and to C-3 by 13.0 Hz.

Table 1 surprisingly reveals very similar chemical shift effects of the lone electron pair at nitrogen in **5** and of the NH bond, a noticeable differential shielding (1.4 ppm) being observed only for the C-8,9 pair. The corresponding position in the imine **12** will be shown in Section D to exhibit the only discernible chemical shift non-equivalence. Such small differential effects are consistent with earlier conclusions[13] from ^{1}H-NMR studies of long-range protonation shifts.



6-(SCS)

7-(SCS)



18-(SCS)

The iminium ion **6** carries a second NH bond in place of a lone electron pair. Assuming the same small effects as in **5** to apply to this replacement, we may ascribe the chemical shift changes observed for **6** mainly to the positive charge as shown in formula **6**-(SCS). They were calculated relative to the averaged values δ of **5** in the absence of NaOH (Table 1). The same reference, **5** with effective C_{2v} symmetry, leads to the chemical shift changes depicted in **7**-(SCS) for the deprotonated imine in THF/ether (3:1); this lithium imide is perhaps a symmetric dimer because it maintains C_{2v} symmetry spectroscopically down to −107°C. The comparison of **6**-(SCS) with **7**-(SCS) should give an impression of the range of electric field effects caused by a change of two units in the formal charge at nitrogen. Assignments posed no problem with **6** and **7**, except for the 4,7- and 5,6-positions which were assumed to conserve the same sequence as in **5**. Indeed, the Δδ ratios of **7**/**6** for corresponding positions are always negative as expected for the sign change of the per-

Table 1. ^{13}C- and some ^{1}H-NMR chemical shifts (δ) for **5** and **8**–**11** in $CDCl_3$

	5[a]	**5**[b]	**8**	**9**	**10**	**11**
T [°C]	+25.0	+29.0	+29.0	-21.7	-33.0	-33.0
1-CH_3	28.6	28.9	27.0	29.7	-[c]	-[d]
(*H*)	1.33[e]	1.38	1.55[f]	1.22[g]	-	-
3-CH_3	29.2	28.9	29.8	29.1	27.7	28.4
(*H*)	1.45	1.38	1.34	1.50[g]	1.47	1.28
C-1	47.7	47.6	46.7	48.3	58.1	60.7
C-2	201.7	201.5	187.1	187.9	186.5	186.2
C-3	47.5	47.6	48.0	49.1	49.4	48.3
C-4	123.0[h]	122.8	122.6	122.8	121.9	122.3
C-5	127.7[i]	127.5	127.2[k]	127.5	127.5	127.2
C-6	127.4[i]	127.5	127.1[k]	127.5	127.5	127.2
C-7	122.9[h]	122.8	122.2	122.3	123.0	122.5
C-8	146.4	147.1	148.6	147.8	149.6	148.9
C-9	147.8	147.1	147.5	146.6	142.6	143.8
ipso	-	-	38.6[l]	149.5	150.0	149.3
ortho	-	-	-	118.9	119.1	116.9
meta	-	-	-	128.2	128.2	128.4
para	-	-	-	122.2	122.1	121.7

[a] Used as SCS reference in $CDCl_3$/2 N NaOH. – [b] Without NaOH. – [c] 10.1 (ethyl CH_3), 35.0 (ethyl CH_2). – [d] 10.7 (ethyl CH_3), 33.6 (ethyl CH_2). – [e] NOE enhancement 11% on N–H, and NOESY. – [f] NOE enhancement 8% on N–CH_3, and NOESY. – [g] In anisole. – [h–k] Assignments with equal labels may be interchanged. – [l] N–CH_3.

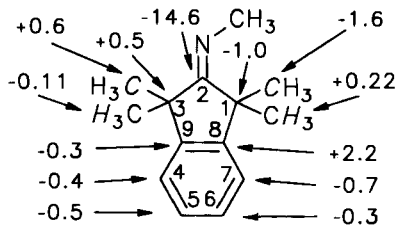
turbing charge. There is no regular decrease of Δδ with increasing distance but rather a remarkable accumulation of opposing charge in the C-8,9 positions beyond the π-isolating centers C-1,3. This situation is reminiscent of the π polarization across space[22] and of Δδ values for the olefinic carbon atoms of 4-substituted cyclopentenes[23], shown for the Grignard derivative **18** for a comparison with **7**-(SCS). The Δδ values for **6** are also roughly comparable to those attributed[24] to the electric field effects in cyclohexanes. The ε positions 4 and 7 experience the smallest changes in **6**-(SCS) and **7**-(SCS) because[25] the π polarizabilities tend to cancel at C-4,7, and their CH bond vectors are perpendicular to the perturbation.

If the Δδ data are tentatively assumed to portray mainly charge distributions, some manifestation of incomplete charge alternation may be gleaned from the five-membered rings in **6**-(SCS) and **7**-(SCS). In both systems, the β and γ atoms are endowed with signs opposite to those of the δ positions. This is no longer the case for SCS by uncharged substituents in Sections C and D where *syn* and *anti* positions will be differentiated.

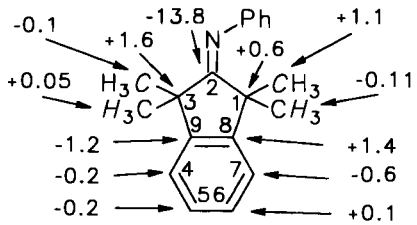
C. Assignments and SCS of *N*-(1,1,3,3-Tetramethyl-2-indanylidene)-amines 8-11

The *N*-methylimine **8** of 1,1,3,3-tetramethyl-2-indanone is the only member of this series showing pairs of sharp ^{1}H- and ^{13}C-NMR singlets for 1- and 3-dimethyl groups at room temperature. In contrast to the imine **5**, the low-field resonance at δ = 1.55 now belongs to the *syn*-dimethyl group (at C-1) with respect to the substituent at nitrogen since it displayed the expected small but distinct intensity enhancement (8%) on irradiation of the *N*-methyl absorption (δ = 3.54). By supporting NOESY experiments also the aromatic protons and by one-bond C/H correlation experiments all of the hydrogen-bearing carbon atoms in Table 1 are identified except for C-5,6. Selective weak $\{^{1}H\}$ irradiation of the 1-CH_3 singlet gave rise to sharpening of the high-field ^{13}C methyl quartet and quaternary C-1 absorptions and also of the low-field component of the C-8/C-9 pair. Conversely, removal of $^{2}J_{CH}$ or $^{3}J_{CH}$ splittings by irradiation of the 3-CH_3 protons (at δ = 1.34) sharpened the 3-CH_3, C-3, and C-9 resonances.

Imines form weak hydrogen bonds with chloroform[26]. To assess the chemical-shift effects, up to two equivalents of the stronger[27] hydrogen-bond donor CH_3OD was added to the $CDCl_3$ solution of **8**, with the result of moving only the C-2 absorption downfield by +1.7 ppm but all others upfield by −0.5 ppm or less. Modest effects were also recognized in other solvents but should usually cancel by subtraction in the SCS values.



8-(SCS)



9-(SCS)

Having noticed the similar influences of the NH bond and of the lone electron pair in Section **B**, we may now use **5** in C_s symmetry (Table 1) as the reference compound for SCS along the C=N bond. For C-3 (γ), 3-CH_3 (δ), C-9 (δ), and the 3-methyl protons (ε) in the *anti*-positions of **8**-(SCS), a weak long-range effect is immediately apparent in the sense of HC and CC polarization caused by the new *N*–CH_3 group. The SCS for corresponding positions at the *syn* side are at least twice as large but all with the opposite signs. Thus, SCS yield more detailed information than statements of simple differential shielding, but comparisons with **7**-(SCS) as an example reveal no general correlation.

The *N*-phenylimines **9**–**11** show separate resonances for almost all carbon atoms at low temperature (Table 1). These

can be partially assigned by careful inspection, firstly of pairwise coalescences above room temperature (see Experimental), and secondly of the (*Z*,*E*) intensity ratio (ca. 4:6) observed for almost every signal pair of **10**/**11**, in accord with the energy difference of 0.3 kcal/mol from molecular mechanics[28]. However, a final differentiation on this basis alone remained difficult owing to small temperature dependences of chemical shifts comparable with some of the shift differences. Since NMR correlation experiments can be troublesome at low temperatures, we used methylation shifts which provide straightforward decisions because every change in going from **9** to **10** and **11** agrees satisfactorily with the analogous step previously reported[29] for the corresponding ketone series.

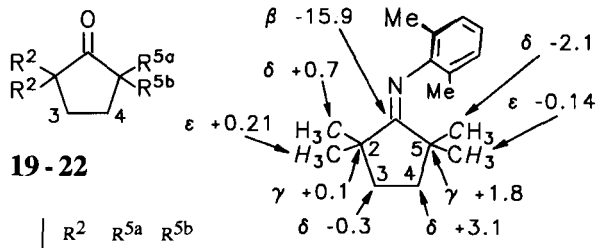
The effects of replacing the imino hydrogen atom in **5** by phenyl are shown in **9**-(SCS) to be partially opposite to those in **8**-(SCS). This phenyl group should be perpendicularly oriented as in the isoelectronic olefin[30] (**9**, HC in place of N), with its π surface facing the *syn*-CH_3 groups. Magnetic anisotropy could therefore explain the upfield ^1H (ε) but not the downfield ^{13}C (γ and δ) shifts of *syn*-CH_3 and of C-1. A later publication will demonstrate similar patterns for the olefinic series.

D. Assignments and SCS of *N*-(2,2,5,5-Tetramethylcyclopentylidene)amines 12–17

The *N*-unsubstituted imine **12**[7,16] had to be cooled below −110°C (coalescence temperature) for the detection of a chemical shift non-equivalence which was found only for C-2/C-5. This reiterates the observation of a similar SCS by the NH bond and the lone electron pair, thus promising too little reward from a similar investigation at higher pH as done for **5**. Moreover, it appeared reasonable to assign C-2,5 in Table 2 by analogy with **5** (Table 1) because the structural difference at C-3,4 is symmetrical with respect to the 2- and 5-positions.

The low-temperature spectrum of **16** in Table 2 showed all of the expected non-equivalences C-2/C-5, 2-CH_3/5-CH_3, and CH_2-3/CH_2-4. The last of these is by far the largest one (3.4 ppm) and must be due to a long-range deshielding effect of the *N*-aryl substituent along the CN double bond because it is absent in **12**. Methylation shifts in the series **13**–**17** were used for unbiased *syn*/*anti* assignments in **16** in the following way.

The series **19**–**22** of methylated cyclopentanones[31,32] in Table 3 demonstrates the operation and magnitude of methyl SCS in the five-membered ring framework. Each additional methyl group causes the usual positive α and β shift increments Δδ. The methyl-induced γ shifts are consistently upfield (ca. −2 ppm) along the CH_2 chain but rather small across the carbonyl center, perhaps due to cancellation of γ and δ effects.



	R^2	R^{5a}	R^{5b}
19	H	H	H
20	Me	H	H
21	Me	Me	H
22	Me	Me	Me

Table 2. ^{13}C- and some ^1H-NMR chemical shifts (δ) for **12**–**17** in $CDCl_3$

	12[a]	**13**	**14**	**15**	**16**	**17**
T [°C]	-117.1	+29.1	+29.0	+29.1	-20.5	-30.0
2-CH_3	27.2	-	26.2	27.2 / 27.6	27.9	-[b]
(*H*)	1.06[c]	-	1.25	1.20 / 1.24[d]	1.27	-
5-CH_3	27.2	-	-	16.4	25.1	25.0
(*H*)	1.06[c]	-	-	0.68[d]	0.92	0.90[d]
o-CH_3	-	17.4	17.5	17.8 / 18.1	18.5	19.1
(*H*)	-	1.92[d]	1.96	1.92 / 1.98[d]	2.04	2.00[d]
C-1	203.0	181.5	186.4	188.1	187.1	186.1
C-2	44.6	35.0	43.2	44.0	44.7	52.8
C-3	36.1	24.4	40.0	37.5	35.8	29.0
C-4	36.1	24.0	20.5[e]	29.9	39.2	39.2
C-5	43.8	31.1	31.2[f]	38.3	45.6	44.6
ipso	-	149.6	149.7	148.8	147.3	147.5
ortho	-	125.1	125.3	123.9 / 126.7	124.8	124.8
meta	-	127.5	127.8	127.6 / 128.1	127.4	127.5
para	-	122.3	122.4	122.4	121.8	121.7

[a] In $CDCl_3/CH_2Cl_2$/diethyl ether. — [b] 9.1 (ethyl CH_3), 29.9 (ethyl CH_2). — [c] At room temperature. — [d] In CCl_4 at room temperature. — [e] Deuteration shift $^2\Delta = -0.10$ ppm. — [f] Deuteration shift $^1\Delta = -0.30$ ppm, $^1J_{CD} = 20$ Hz.

Table 3. ^{13}C-NMR chemical shifts (δ) for **19**–**22** in $CDCl_3$

	19[a]	**20**[b]	**21**[c]	**22**[c]
C-1	218.8	223.8	224.1	226.4
C-2	38.4	44.9	44.7	45.2
C-3	23.8	38.5	36.6	34.9
C-4	23.8	18.7[d]	28.0	34.9
C-5	38.4	37.1[e]	43.1	45.2
2-CH_3	-	23.7	24.1 / 24.8	24.9
5-CH_3	-	-	15.2	24.9

[a] From ref.[31]. — [b] This work, compare ref.[31]. — [c] From ref.[32]. — [d] Deuteration shift $^2\Delta = -0.12$ ppm. — [e] Deuteration shift $^1\Delta = -0.32$ ppm, $^1J_{CD} = 20.4$ Hz.

For compounds **14** and **15** with unequal degrees of substitution at their 2- and 5-positions, only one stereoisomer was observed which must have the *E* configuration according to empirical substituent constants[20]. Therefore, the ^{13}C-NMR *syn*/*anti* assignments in Table 2 with respect to the *N*-aryl groups emerge from comparisons of the methylation shifts for the pairs **13**/**14** and **14**/**15** with those of **19**/**20** and

20/21; they agree with independent differentiation of the three CH_2 groups in **14** by isotope-induced shifts[33] (upfield counted as negative[33]) after α deuteration. The 2,2-diethyl-5,5-dimethyl derivative **17** was also observed in only one form and provides a final verification of the assignments in **16** by the clearly identifiable methylation shifts of C-2 (β) and C-3 (γ).

The 2,6-dimethylphenyl substituent in **16** is doubtlessly orthogonal to the C=N double-bond plane, judging from the structure[3] of the *p*-hydroxy derivative. The most surprising upfield ^{13}C (van-der-Waals) shift of *syn*-methyl in **16**-(SCS) as compared to **9**-(SCS) may be a consequence[34,35] of the two *ortho*-methyl groups of **16** at short distances[3] of ca. 3.5 Å, but the *anti*-CH_3 shift change in **16**-(SCS) is more positive (downfield) than in **9**-(SCS); those SCSs change in the opposite directions for C-5 (*syn*) and C-2 (*anti*). Introduction of the two *ortho*-methyl groups had very little effect in related *N*-(cyclohexylidene)-[36] and *N*-(1-phenylethylidene)anilines[37]. The strikingly different CH_2 values (δ position) in **16**-(SCS) cannot be ascribed to a proximity interaction; such δ effects and the corresponding ones of C-8,9 in **8**-(SCS) and **9**-(SCS) are sufficiently large so as to define a touchstone of theoretical models because their magnitudes are comparable to the recently described[33] β-SCS dependence on chemical shifts.

E. Conclusion and Application

N-Unsubstituted imines (**5** and **12**) show similar effects of the lone electron pair and of the N–H bond on ^1H- and ^{13}C-NMR chemical shifts. Their NMR assignments permit the evaluation of substituent-induced chemical shifts (SCS) along the C=N bond of geometrically well-defined imines as gauges for theoretical models. Electric field and van der Waals effects appear to be operative with roughly comparable efficiency.

The *N*-methyl in **8**-(SCS) and *N*-phenyl substitutents in **9**-(SCS) cause characteristically different SCS patterns; numerically similar values are only observed for long-range effects on the aromatic C-4 to C-9 atoms (δ, ε, and ζ positions) of the 2-indanylidene fragment. Considering the usual analytical uncertainties of experimental ^{13}C-NMR spectra, the propagated errors should be approximately ±0.3 ppm; but the less informative differential shielding expressed by the numerical differences between chemically analogous positions within the same molecule is of course much more precise (ca. ±0.1 ppm). Nevertheless, the existence of appreciable long-range *trans* effects becomes clear from all examples. On the other hand, the usual[38] strong upfield shift of *syn*-γ carbon atoms bearing hydrogen gets much weaker for the quaternary center C-1 in **8**-(SCS); but with aryl as the perturbing substituent, it is replaced by small *downfield* effects on C-1, which are comparable to those for the *anti*-γ nuclei by inspection of **8**-(SCS), **9**-(SCS), and **16**-(SCS).

For a final demonstration how to use SCS, we now derive ^1H- and ^{13}C-NMR assignments for the (*Z*)-bis(imine) **26**. This is trivial[39] by symmetry for the (*E*)-isomer **23** and leads to the hypothetical parent compound **24** by the application of data obtained from **8**-(SCS), assuming simple additivity of the SCS effects. Further use of **8**-(SCS) in the step from **24** to **25** produces δ values which agree reasonably well with the experimental[39] shifts in **26**, considering the bond angle differences from **8**.

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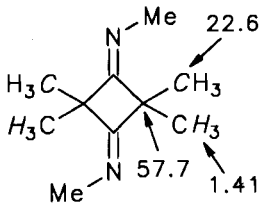
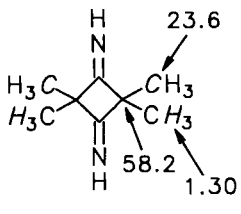
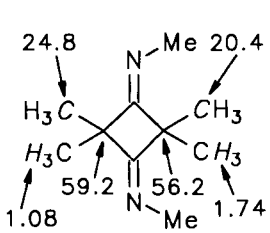


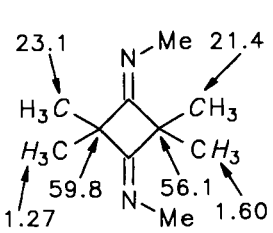
23 (exp.[39])



24 (hypoth.)



25 (calcd.)



26 (exp.[39])

Experimental

IR: Perkin-Elmer 125 or Bruker IFS-45. – UV/Vis: PRQ 20 (C. Zeiss). – NMR: Varian VXR-400S, XL-100-IL, and A-60, or Bruker WP-80-CW and WP-80-DS, internal standard TMS. ^{13}C-NMR multiplicities were taken from off-resonance or gated decoupling.

2-(Hydroxyimino)-1,1,3,3-tetramethylindan (**3**): A 1-l flask was charged with 35.0 g (186 mmol) of crude 1,1,3,3-tetramethyl-2-indanone[8] (**2**), 40.0 g (576 mmol) of hydroxylammonium chloride, 60 ml of dist. water, 250 ml of ethanol (95%), and 100 ml of 2 N NaOH. The product **3** began to separate after 1 d from the refluxing solution. After refluxing for only 2 d and subsequent chilling, the crude product (30.7 g) was filtered by suction and washed with water. Treatment with a large amount of hot hexane or better recrystallization from ethanol yielded 26.6 g (70%) of colorless needles, m.p. 169–171°C (ref.[7] 169–170°C). – ^1H NMR (CCl_4): δ = 1.46 and 1.63 (2 s, 1- and 3-CH_3), 7.08 (s, C_6H_4), 9.18 (br s, OH). – ^{13}C NMR ($CDCl_3$): δ = 26.2 and 30.4 (1- and 3-CH_3), 46.3 and 47.4 (C-1,3), 122.4 (C-4,7), 127.5 and 127.7 (C-6,5), 147.3 and 148.3 (C-9,8), 174.7 (C-2).

2-Imino-1,1,3,3-tetramethylindan (**5**): Dioxane[9] (40 ml) is the most suitable solvent for dissolving the oxime **3** (3.25 g, 16.0 mmol) as well as part of the aqueous solution (33.0 ml, 38.3 mmol) of $TiCl_3$ (15% in 10% hydrochloric acid). The reagents were combined under argon and stirred at 20°C for 95 min. The purple mixture was poured into 150 ml of dist. water and extracted with ether (4 x 25 ml) to yield 0.22 g of a mixture of ketone **2** and oxime **3** in a 1:8 ratio. As soon as possible, 250 ml of ice-cooled 2 N NaOH was added to the acidic phase containing **5** until strongly alkaline. Despite a voluminous blue precipitate, this phase was extracted with ether (4 x 40 ml). The combined ethereal extracts were washed with water (1 x 20 ml), 2 N sodium carbonate (20 ml), and then only two

times with water (20 ml) to keep the pH above 8–9. After drying with magnesium sulfate, the ether was evaporated to give 2.65 g (89%) of pure **5** with m.p. 50–56°C. Recrystallization from hexane was possible at −70°C, but the analytical sample was prepared by treatment of the hydrochloride **6** with 2 N NaOH/ether and ether extraction as above; m.p. 62–64°C in a closed capillary under argon (ref.[7] 68–70°C). – IR (KBr): $\tilde{\nu}$ = 3215 cm^{-1} (sharp NH); 2963, 2924, 2862 (CH); 1670, 1664 (C=N); 1481, 756. – ^1H NMR (CCl_4/NaOH): δ = 1.32 (s, 1-CH_3), 1.43 (s, 3-CH_3), 7.13 (dm, 7-H), ca. 7.20 (mc, 4- to 6-H), 9.35 (br, NH). – ^1H and ^{13}C NMR ($CDCl_3$): Table 1; coupling constants $^1J_{CH}/^3J_{CH}$ (Hz): q 128/q 4.6 (1- and 3-CH_3), dm 157 (C-4,7), d 160/d ca. 7 (C-5,6); $^3J_{CH}$: d 7.5/d 1.5 (C-1), d 13.0/d 0.8 (C-3), t ca. 7 (C-8,9); $^2J_{CH}$ = 9.9 Hz (d, C-2). – ^{13}C NMR (CCl_4/NaOH): δ = 28.6 (1-CH_3), 29.3 (3-CH_3), 47.1 and 47.4 (C-3,1), 122.7 and 122.9 (C-7,4), 127.2 and 127.5 (C-6,5). – ^{13}C NMR (THF/diethyl ether 3:1 at pH = 11): δ = 28.6 (1-CH_3), 29.3 (3-CH_3), 47.6 and 47.7 (C-3,1), 123.2 (C-4,7), 127.6 and 127.8 (C-6,5), 147.5 and 148.6 (C-9,8), 199.5 (C-2).

$C_{13}H_{17}N$ (187.3) Calcd. C 83.37 H 9.15 N 7.48
Found C 83.30 H 9.30 N 7.34

The recommended[9] addition of ammonium acetate or of aqueous (50%) acetic acid led to increased hydrolysis and was abandoned. It is important to avoid washing of the ethereal extracts to neutrality because **5** is sufficiently basic to be extracted into neutral water. Accordingly, **5** can quickly absorb HCl from the laboratory air.

(1,1,3,3-Tetramethyl-2-indanylidene)ammonium chloride (**6**): A solution of 0.27 ml (3.4 mmol) of conc. HCl in 1.5 ml of 99% ethanol was added slowly to 600 mg (3.20 mmol) of **5** in 3 ml of 99% ethanol at 0°C. The copious precipitate was diluted with 5 ml of ether to decrease solubility, washed thoroughly with ether to neutrality by suction and dried in vacuo with P_2O_5 present. The colorless powder (543 mg, 81%) showed a crystal transformation at 213°C and sublimed up to 288°C. Very slow hydrolysis was observed for **6** in 2 N HCl in the course of several days at ambient temperature. – IR (nujol): $\tilde{\nu}$ = 2725 cm^{-1}, 1705, 1570. – ^1H NMR ($CDCl_3$): δ = 1.82 (s, 4 CH_3), 7.25 and 7.37 (AA'MM' spectrum, C_6H_4), 13.95 (br, NH_2). – ^{13}C NMR ($CDCl_3$): δ = 28.5 (qq, ^1J = 130, ^3J = 4.5 Hz, 4 CH_3), 49.7 (m, ^3J = 3.2 Hz, C-1,3), 122.6 (dm, ^1J = 159 Hz, C-4,7), 129.0 (dd, ^1J = 161, ^3J = 7 Hz, C-5,6), 143.8 (m, ^3J = 3.5 Hz, C-8,9), 215.9 (unresolved, C-2).

$C_{13}H_{18}ClN$ (223.7)
Calcd. C 69.79 H 8.11 Cl 15.84 N 6.26
Found C 69.76 H 8.25 Cl 15.73 N 5.84

2-(Lithioimino)-1,1,3,3-tetramethylindan (**7**): A solution of 1.28 g (6.83 mmol) of imine **5** in 9 ml of dry THF was ice-cooled in a 50-ml two-necked flask under streaming argon. With magnetic stirring and connection to a gas buret, 4.40 ml (7.03 mmol) of 1.6 M ethereal methyllithium was added within 20 min as long as methane was liberated. The slightly yellow and turbid solution of **7** was stable at 25°C and showed only traces of impurities. Compound **7** remained dissolved down to −107°C but was insoluble in pure ether. – ^1H NMR (THF/diethyl ether 3:1 at +25°C): δ = 1.14 (s, 1- and 3-CH_3), 7.05 and 7.17 (AA'MM' spectrum, C_6H_4), no changes at −47 and −107°C. – ^{13}C NMR (THF/diethyl ether 3:1 at +25°C): δ = 29.7 (qq, ^1J = 125.5, ^3J = 5 Hz, 1- and 3-CH_3), 46.8 (s, C-1,3), 123.6 (dm, ^1J = 155 Hz, C-4,7), 125.8 (dm, ^1J = 157 Hz, C-5,6), 151.7 (s, C-8,9), 178.3 (br s, C-2); upfield shifts down to −107°C by 2.6 ppm for C-2 and by ca. 0.7 ppm for CH_3, C-1,3 and C-8,9 without any further splitting.

N-(1,1,3,3-Tetramethyl-2-indanylidene)methylamine (**8**): Freshly distilled methylamine (14 or 30 ml, 317 or 680 mmol) was condensed into 30 ml of dry toluene cooled in the reaction flask at −65°C under nitrogen. A solution of 3.76 g (20 mmol) of ketone **2**[8] in 10 ml of dry toluene was introduced and 5.50 or 11.0 ml (50 or 100 mmol) of $TiCl_4$ in 10 ml of dry toluene added dropwise with stirring. A voluminous, orange-colored precipitate formed on warming to room temp. when excess methylamine had vaporized. It was diluted with 100 ml of dry toluene and heated to 150°C at a reflux condensor for 2 h. Titanium salts were filtered off by suction, and the solvent was evaporated to yield 2.90 g (72%) of colorless **8**; m.p. ca. 20°C, b.p. 110–112°C/10 Torr or 122–126°C/12 Torr. Purification was also possible by dissolving **8** in 2 N HCl, alkalization and extraction with ether. – IR (film): $\tilde{\nu}$ = 3020 cm^{-1}, 2960, 2920, 2860; 1688, 1683 (C=N); 1487, 1452, 755. – UV (Cyclohexane): λ_{max} (lg ε) = 258 nm (2.942), 265 (3.123), 272 (3.163). – ^1H NMR (CCl_4): δ = 1.28 (s, 3-CH_3), 1.50 (s, 1-CH_3), 3.47 (s, NCH_3), 7.12 (s, C_6H_4). – ^1H NMR ($CDCl_3$): δ = 1.34 (s, 3-CH_3), 1.55 (s, 1-CH_3), 3.54 (s, NCH_3), 7.15 (dm, 7-H), 7.18 (mc, 4-H), ca. 7.24 (m, 5,6-H). – ^{13}C NMR ($CDCl_3$): Table 1; coupling constants $^1J_{CH}/^3J_{CH}$ (Hz): q 127.5/q 4.5 (1- and 3-CH_3), q 134 (NCH_3), dm 158 (C-4,7), dm 160 (C-5,6).

$C_{14}H_{19}N$ (201.3) Calcd. C 83.53 H 9.51 N 6.96
Found C 83.04 H 9.26 N 7.02

N-(1,1,3,3-Tetramethyl-2-indanylidene)aniline (**9**): The procedure used for the preparation of **10/11** was followed in the $TiCl_4$-mediated condensation of ketone **2**[8] with aniline, but heating to 185°C was stopped after 4 h. Recrystallization from ligroin gave 17% of very fine needles, m.p. 124–125°C (ref.[15] 119.5–122°C). – IR (KBr): $\tilde{\nu}$ = 3060 cm^{-1}, 2985, 2967, 2925, 2862, 1683, 1598, 1484, 762, 754, 701. – UV (Cyclohexane): λ_{max} (lg ε) = 235 nm (4.140), 260 (3.182), 266 (3.360), 272 (3.440), 280 (sh 3.120), 302 (sh 2.859). – ^1H NMR (CCl_4): δ = 1.33 (br s, 4 CH_3), 6.65 (dm, ^3J = 8 Hz, *o*-H), 7.12 (mc). – ^{13}C NMR ($CDCl_3$, +51°C): δ = 29.5 (q, 1- and 3-CH_3), 48.6 (s, C-1,3), 118.5 (d, 2 *o*-C), 121.8 (d, *p*-C), 122.1 (d, C-4,7), 127.2 (d, C-5,6), 127.6 (d, 2 *m*-C), 147.5 (s, C-8,9), 150.1 (s, *ipso*-C), 186.2 (s, C-2); coupling constants $^1J_{CH}/^3J_{CH}$ (Hz) at −22.3°C: qm 128 (1- and 3-CH_3), d 160/t 6 (*o*-C), d 160/t 7 (*p*-C), dm 159 (C-4,7), dd 160 (C-5,6), d 159/d 8 (*m*-C), t 8 (*ipso*-C).

$C_{19}H_{21}N$ (263.4) Calcd. C 86.65 H 8.04 N 5.32
Found C 86.39 H 7.94 N 5.74

N-(1,1-Diethyl-3,3-dimethyl-2-indanylidene)aniline (**10** and **11**): $TiCl_4$ (0.73 ml, 6.6 mmol) was added to ice-cooled aniline (7.22 ml, 79 mmol), which was stirred under argon in a 25-ml Schlenk flask equipped with a reflux condensor. The resulting deeply colored suspension was warmed to room temperature. After 10 min, a solution of 480 mg (2.2 mmol) of 1,1-diethyl-3,3-dimethyl-2-indanone[29] in 3 ml of aniline was added at once and the mixture heated to 180°C under argon for 22 h. Since the product **10/11** was not soluble in dilute aqueous acid, most of the aniline could be removed by extraction from 50 ml of petroleum ether with two batches (25 ml) of 2 N HCl. The organic layer was washed with distilled water and dried with Na_2SO_4 to yield 580 mg of crude oil containing some residual ketone. Chromatography on SiO_2 (Woelm, activity I, 5.5 g) with dry CCl_4 gave 248 mg (38%) of **10/11** of sufficient purity to be recrystallized from methanol (2 ml) at −78°C. M.p. 70.5–72.5°C; b.p. 100–140°C (bath temp.)/0.001 mbar. – IR (KBr): $\tilde{\nu}$ = 2969 cm^{-1}, 2876, 1689, 1671, 1595, 1483, 1454, 1376, 1220, 1027, 764, 696. – UV (cyclohexane): λ_{max} (lg ε) = 265 nm (3.368), 272 (3.442), 300 (2.850, broad). – ^1H NMR ($CDCl_3$, +20°C at 360 MHz or −40°C at 60 MHz): δ = 0.67 and 0.73 (2 t, ethyl CH_3 of *Z* and *E*), 1.28 and 1.47 (s, 3-CH_3 of *E* and *Z*), 1.57, 1.73, 1.82, and 2.03 (diastereotopic CH_2), 6.80 (d, 2 *o*-H), 7.00 (t, *p*-H), 7.09 and 7.15 (broad, *m*-H), 7.28 (m, C_6H_4). – ^{13}C

NMR ($CDCl_3$ at +40 or +51°C): δ = 10.2 (q, ethyl CH_3), 28.4 (q, 1,3-CH_3), 34.2 (t, CH_2), 49.0 (s, C-3), 59.6 (s, C-1), 118.0 (d, *o*-C), 122.4 (d, C-4 and *p*-C), 122.6 (d, C-7), 127.4 (d, C-5,6), 128.4 (d, *m*-C), 143.6 (s, C-9), 150.1 (s, C-8), 150.2 (s, *ipso*-C), 185.9 (s, C-2); compare Table 1. (*Z*,*E*) Coalescences (Δν in Hz) in $CDCl_3$ at 25.15 MHz: Ca. +35°C (64, C-1), ca. +30°C (54, *o*-C), +23°C (35, CH_2 and 30, C-9 and 27, C-3), +19°C (16, ethyl CH_3), ca. +16°C (18, 3-CH_3 and 9, C-2); average $\Delta G^{\neq}$ = 14.9 (±0.2) kcal/mol.

$C_{21}H_{25}N$ (291.4) Calcd. C 86.55 H 8.65 N 4.81
Found C 86.39 H 8.66 N 4.69

2,2,5,5-Tetramethylcyclopentaneimine (**12**)[7,16]: ^{13}C NMR ($CDCl_3$/CH_2Cl_2 at +24°C): δ = 27.0 (qq, ^1J = 126, ^3J = 4.5 Hz, CH_3), 36.2 (tm, ^1J = 130, ^3J = 4.0 Hz, CH_2), 43.8 (m, C-2,5), 201.5 (C-1); compare Table 2.

N-(2,2-Dimethylcyclopentylidene)-2,6-dimethylaniline (**14**): A solution of 5.50 g (49 mmol) of 2,2-dimethylcyclopentanone (**20**), 7.20 ml (58 mmol) of 2,6-dimethylaniline, and 100 mg of PCl_5 in 30 ml of toluene was heated to 135°C in a water-separator for 24 h. The solvent and residual amine were removed in vacuo, and 3.70 g (35%) of **14** distilled slowly above 140°C (bath temp.)/12 Torr. Much lower yields were obtained with $TiCl_4$ in place of PCl_5. The analytical sample was prepared from the hydrogen tetrafluoroborate of **14** (see below) in 88% yield. – IR (film): $\tilde{\nu}$ = 3065 cm^{-1}, 3015, 2955, 2860, 1683, 1461, 1096, 761. – UV (cyclohexane): λ_{max} (lg ε) = 275 nm (3.142), 281 (3.132). – ^1H NMR (CCl_4): δ = 1.23 (s, 2-CH_3), 1.70 (mc, CH_2-3,4), 1.87 (m, CH_2-5), 1.92 (s, *o*-CH_3), 6.70 and 6.84 (aromat. AB_2). – ^{13}C NMR ($CDCl_3$): δ values at −50°C equal to those in Table 2; coupling constants $^1J_{CH}/^3J_{CH}$ (Hz): t 129.5/m 4 (C-3), tm 132 (C-4), t 129/t 4 (C-5), q 126/q 4.5 (2-CH_3), q 127/d 5 (*o*-CH_3), dm 155 (*m*-C), d 159 (*p*-C).

$C_{15}H_{21}N$ (215.3) Calcd. C 83.67 H 9.83 N 6.51
Found C 83.21 H 9.55 N 6.81

370 mg of **14** was deuterated with one equivalent of CH_3OD in $CDCl_3$ at room temp. ($t_{1/2}$ ca. 3 d); see Table 2.

N-(2,2-Dimethylcyclopentylidene)-2,6-dimethylanilinium Tetrafluoroborate (**14** · HBF_4): The crude product **14** obtained from 36 mmol of **20** was precipitated with 5.4 ml (38 mmol) of ice-cooled 50% aqueous HBF_4 to yield 1.53 g (14%) of the salt; m. p. 208.5–209°C (from 5 ml of ethanol). – IR (KBr): $\tilde{\nu}$ = 2965 cm^{-1}, 2560 (very br), 1674, 1467, 1083 (BF_4). – ^1H NMR (CH_2Cl_2/$CDCl_3$): δ = 1.62 (s, 2-CH_3), 2.02 (mc, CH_2-3,4), 2.19 (s, *o*-CH_3), 2.52 (mc, CH_2-5), ca. 7.22 (mc, 3 aromat. H).

$C_{15}H_{22}BF_4N$ (303.2) Calcd. C 59.43 H 7.32 N 4.62
Found C 59.03 H 7.34 N 4.83

2,6-Dimethyl-N-(2,2,5,5-tetramethylcyclopentylidene)aniline (**16**): ^1H NMR (−49°C in $CDCl_3$/CCl_4, 1:2): δ = 0.92 (5-CH_3), 1.27 (2-CH_3), 1.68 (s, CH_2-3,4), 2.04 (s, *o*-CH_3), 6.80 and 6.93 (aromat. AB_2). – ^{13}C NMR ($CDCl_3$, +28.5°C): δ = 18.4 (q, *o*-CH_3), 26.7 (br, q, 2- and 5-CH_3), 37.8 (br, t, CH_2-3,4), 45.3 (s, C-2,5), 121.8 (d, *p*-C), 124.7 (s, *o*-C), 127.5 (d, *m*-C), 147.7 (s, *ipso*-C), 186.6 (s, C-1); compare Table 2.

N-(2,2-Diethyl-5,5-dimethylcyclopentylidene)-2,6-dimethylaniline (**17**): Imine **14** (1.10 g, 5.1 mmol) and diisopropylamine (0.35 ml, 2.50 mmol) in 30 ml of dry THF were stirred at −60°C under nitrogen. *n*-Butyllithium (4.0 ml, 5 mmol) in hexane was added dropwise and the solution warmed to +3°C for 15 min with subsequent dropwise addition of 0.4 ml (5.0 mmol) of ethyl iodide. The solution was warmed up to room temp., fading within 25 min to pale yellow. As one repetition of this cycle was not sufficient to peralkylate **14**, the alternating treatment with butyllithium and ethyl iodide had to be repeated thrice. Workup with water and ether gave 1.10 g (80%) of a yellow oil, b.p. 110–130°C (bath temp.)/0.05 Torr. – IR (film): $\tilde{\nu}$ = 2955 cm^{-1}, 2870, 1673, 1460, 760. – UV (cyclohexane): λ_{max} (lg ε) = 238 nm (4.026), 282 (3.197). – ^1H NMR (CCl_4): δ = 0.90 (s, 5-CH_3), 0.93 (t, *J* = 7 Hz, ethyl CH_3), 1.60 (mc, CH_2-3,4 and ethyl CH_2), 2.00 (s, *o*-CH_3), 6.69 and 6.82 (*p*- and *m*-H). – ^{13}C NMR ($CDCl_3$, +32°C): δ similar to Table 2, except for CH_2-3 (29.6) and *ipso*-C (148.1).

$C_{19}H_{29}N$ (271.5) Calcd. C 84.07 H 10.77 N 5.16
Found C 83.78 H 10.52 N 5.49

2,2-Dimethylcyclopentanone (**20**): Some improvements and shortcuts of the literature procedure were developed. γ-Butyrolactone was treated with lithium diisopropylamide and methyl iodide to give α,α-dimethyl-γ-butyrolactone which underwent ring opening on treatment with PBr_5 to afford ethyl 4-bromo-2,2-dimethylbutanoate[40,41]. This ester was added to sodium diethyl malonate in ethanol and the alkylation[41] accelerated by the addition of dry DMF to permit a reflux temperature of 112°C (20 h). The triester[40,41] obtained hydrolyzed slowly at 130°C in conc. HCl; solvents were removed by distillation up to 180°C when decarboxylation started. The resulting 2,2-dimethyladipoic acid[40,42] was cyclized[43] to the anhydride[40,43] and decarboxylated to yield raw **20** (up to 26% over five steps); b.p. 143–146°C (ref.[43] 143°C).

400 mg of **20** was deuterated in a mixture of 1.8 ml of $CDCl_3$ and 0.15 ml of CH_3OD at ambient temp. ($t_{1/2}$ ca. 2 d) and distilled. – ^{13}C NMR ($CDCl_3$): Table 3.

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