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Demonstration of the Nitrogen Inversion Mechanism of Imines in a Schiff Base Model ☆

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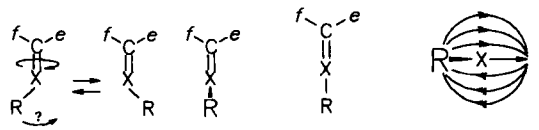
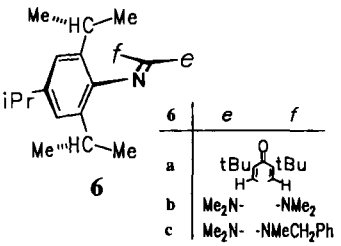
Experimental differentiation between pure C=N double bond rotation and nitrogen inversion in *N*-arylimines is possible with a single compound (**13b**) under the proviso of slow rotation about the *N*-aryl single bond. Labelling by ^1H and ^{13}C nuclei at the diastereotopic faces of the C=N moiety as well as of the *N*-aryl group is the clue to a successful stereodynamic analysis, as performed by variable-temperature NMR spectroscopy of **13b**, a sterically congested and chiral model compound. Interpretation of similar measurements on a second model (**13d**) is less straightforward. The experimental observation of time-averaged C_s symmetry by NMR coalescences is only compatible with a mechanism of (*E/Z*) stereomutation either by pure inversion at sp^2 nitrogen or by a contribution from C=N rotation together with a synchronized (geared) contrarotation about the *N*-aryl single bond. However, the latter combination is concluded to be predominantly inversion-like by comparisons with related imines.

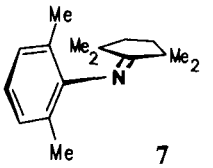
The conformational lability at a C=X double bond in **1** and **2** is measured by the rate of (*E,Z*) diastereoisomerization, or of (*E,Z*) diastereotopomerization if the substituents *e* and *f* are constitutionally equal. This stereomutation might occur by a 180°-rotation about the C=X double bond via a transition state **3**; but if the key atom X carries a lone electron pair (like X = N or C^-Li^+), the alternative mechanism of "planar" inversion (or "lateral shift"[2]) is more probable with linear coordination of X in a transition state **4**. Quantum-mechanical calculations on imines (X = N) indicate a much higher energetic barrier of rotation (**3**) than of inversion (**4**) for iminomethane (**1**, R = *e* = *f* = H)[3-6] and for *N*-methyleneaniline[7]. Combinations of these mechanistic alternatives are conceivable[2,8], as shown by the elliptical movements in a projection **5** along the X=C bond, but these are not supported by the calculations[5,9]. Neither would it be possible to demonstrate their existence by means of NMR spectroscopy which is sensitive to the final configurations and the rate of their interconversion only, but not to the intermediate mechanistic details.



1 **2** **3** **4** **5**

Definite experimental evidence to differentiate between these mechanisms has apparently not been published. The methyl groups within each one of the *o*-isopropyl substituents are diastereotopic (inequivalent) in the ground state of the quinone imine **6a** and should become enantiotopic (equivalent by mirror symmetry) during inversion (**4**); but the attempt to demonstrate this was thwarted by faster rotation about the N-aryl single bond[10,11] which leads to premature positional equilibration of these methyl groups. Kessler and Leibfritz[11] had to use guanidines to show that the diastereotopomerization of the groups *e* and *f* in **6b** occurred as fast as isopropyl enantiotopomerization; but comparisons with **6c** and further derivatives were required to exclude contributions from N-aryl single-bond rotation in **6b**.





Thus all available evidence accumulates to a "consensus"[12] with "many arguments"[13] for the inversion mechanism of imine stereomutation. However, comparisons within a series of related compounds would be time-consuming in other systems[13] (e. g., X = C^-Li^+) and may be quantitatively questionable for reasons of possible electronic[3] and conformational[7] differences in the ground states. Guided by synthetic and kinetic experience[14,15] with the conformationally quite rigid imine **7**, we therefore considered the construction of a model Schiff base which would permit such mechanistic differentiation in a single compound rather than in a series.

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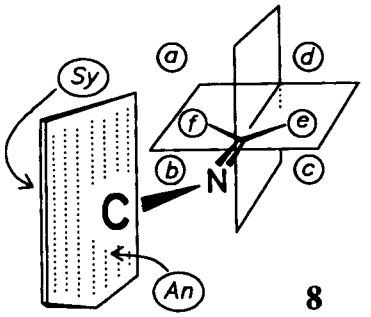
A. Design and Syntheses of the Model Compounds

A mechanistic differentiation between C=N double bond rotation and inversion is experimentally not possible without the guaranty of slow N–aryl single-bond rotation, as exemplified above and detailed in the schematic sketch **8**.

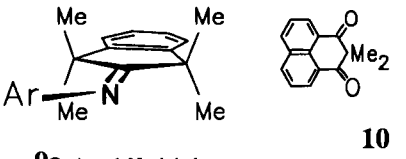


8

The novel features in **8** consist in a discrimination of the four octants, *a*–*d*, about the carbon terminus of the N=C double bond by a non-axially symmetric substituent at the nitrogen atom. The latter substituent defines a plane of chirality with diastereotopic faces *An* and *Sy* which are designated[16] according to their *syn* and *anti* relations to the X=C double bond. Inversion at nitrogen via transition state **4**, if sufficiently fast on the NMR time scale, will coalesce (equalize) the following NMR signals of **8**: *a* = *d*, *b* = *c*, *e* = *f*, and *An* = *Sy*, which amounts to time-averaged symmetry C_s. Pure N=C double-bond rotation will *not* exchange the diastereotopic *N*-aryl faces if the dihedral angle (ca. 90°) at the C–N single bond is conserved during this motion. This leads to time-averaged symmetry C_2: *a* = *c*, *b* = *d*, *e* = *f*, but *An* ≠ *Sy* (see also **15** for a more specific representation). Therefore, constitutionally identical reporter groups (methyl substituents) in the four octants *a*–*d* should have resolvable NMR shift differences; and if their spatial assignments were known, they would immediately reveal which mechanisms operates. The absence of aryl–N single-bond rotation is of fundamental importance for these analyses and may be monitored by the permanently different NMR signals for *a* ≠ *b* and for *c* ≠ *d*. Such aryl–N rotation was not sufficiently slow[17] in the *N*-(1-naphthyl)imine **9a** and thus caused the collapse of all four methyl signals (*a* = *b* = *c* = *d*) to one singlet in the high-temperature NMR spectrum. Hence, an additional substituent is required in the β-position of the naphthyl group of **9a** to prevent this single-bond rotation.

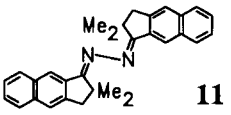
The necessity of knowing absolute spatial assignments for the reporter groups *a*–*d* is very inconvenient, however. To circumvent this requirement, we finally append to **8** diastereotopic groups at the *N*-substituent which report on the *An* and *Sy* half-spaces. All of the previously explained topological relations remain valid, but pure N=C double-bond rotation can now also be recognized directly by conservation of the difference of such diastereotopic faces (*An* ≠ *Sy*), while inversion is revealed by face equalization (*An*,*Sy* coalescence).

Syntheses of the suitable *N*-substituent started with the known[18] preparation of 2,2-dimethyl-2*H*-benz[*f*]indene-1,3-dione (**12a**) from dimethylmalonyl dichloride and naphthalene. Unfortunately, the isomeric 2,2-dimethyl-1*H*-phenalene-1,3(2*H*)-dione (**10**) was always found as a major contaminant (34–45%) despite our efforts to suppress it by variation of the reaction time and temperature (–18 to +70°C) in dichloromethane or 1,2-dichloroethane. Chromatographic separation was not effective, and **12a** could be purified only by fractional crystallization from cyclohexane. The hydrocarbon **12b** was quantitatively formed by Wolff-Kishner reduction of **12a**; if any azine **11** was isolated, this could be recycled to give also **12b**.

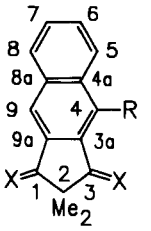


9a: Ar = 1-Naphthyl
b: Ar = Phenyl

10



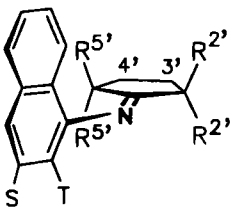
11



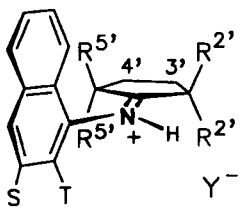
12

12	R	C=X
a	H	C=O
b	H	CH_2
c	Br	CH_2
d	Li	CH_2
e	NH_2	CH_2

Since treatment of **12b** with a nitration mixture or with copper dinitrate in acetic anhydride resulted in unidentified mixtures of products, the 4-amino derivative **12e** had to be prepared by a synthetic detour. The use of one equivalent of bromine or of BrI in $CHCl_3/CCl_4$ solvent at or below room temperature gave the monobromide **12c** always accompanied by 4,9-dibromo-2,3-dihydro-2,2-dimethyl-1*H*-benz[*f*]indene, but the reaction with one equivalent of *N*-bromosuccinimide in DMF[19] afforded **12c** almost exclusively. The lithium derivative **12d** was generated from **12c**



13



14

13, 14	$R^{2'}$	$R^{5'}$	S	T	Y
a	H	H	$CH_2CMe_2CH_2$		-
b	Me	Me	$CH_2CMe_2CH_2$		ClO_4
c	H	H	H	Me	-
d	Me	Me	H	Me	BF_4
e	Me	H	H	Me	BF_4
f	Me	CD_3	H	Me	BF_4

by Br/Li exchange; it reacted with diphenylphosphoryl azide to furnish an intermediate phosphoryltriazene[20] and, by competing proton transfer, the hydrocarbon **12b**. The triazene was reduced in situ to the amine **12e**, which was then transformed via imine **13a** into the final product **13b** by permethylation according to the reported[14] procedures. By the latter method, the 2-methylnaphthylimines **13d** and **13f** were prepared from **13c** and **13e**, respectively. The crystalline hydrogen perchlorate **14b** served well for the purification and elemental characterization of **13b**; but only the hydrogen tetrafluoroborate **14e** could be used in this manner, whereas **14f** and **14d** were found to dissociate too readily due to the low basicity of the imines **13f** ([D_6]**13d**) and **13d**.

B. Performance of the Model Compounds

The full stereopicture **15** displays the imine **13b** with the perpendicular conformation of the *N*-aryl substituent, as inferred from the X-ray analysis[21] of the *p*-hydroxy derivative of **7**. A low-temperature NMR spectrum of the aliphatic protons of **13b** (bottom trace of Figure 1) shows 6 widely spread singlets for the methyl groups at the cyclopentylidene moiety (*a*–*d* in **8** or **15**) and at the *N*-aryl function (*An* and *Sy* 2-CH_3 in **15**). The CH_2 (*e*, *f*) groups at cyclopentylidene

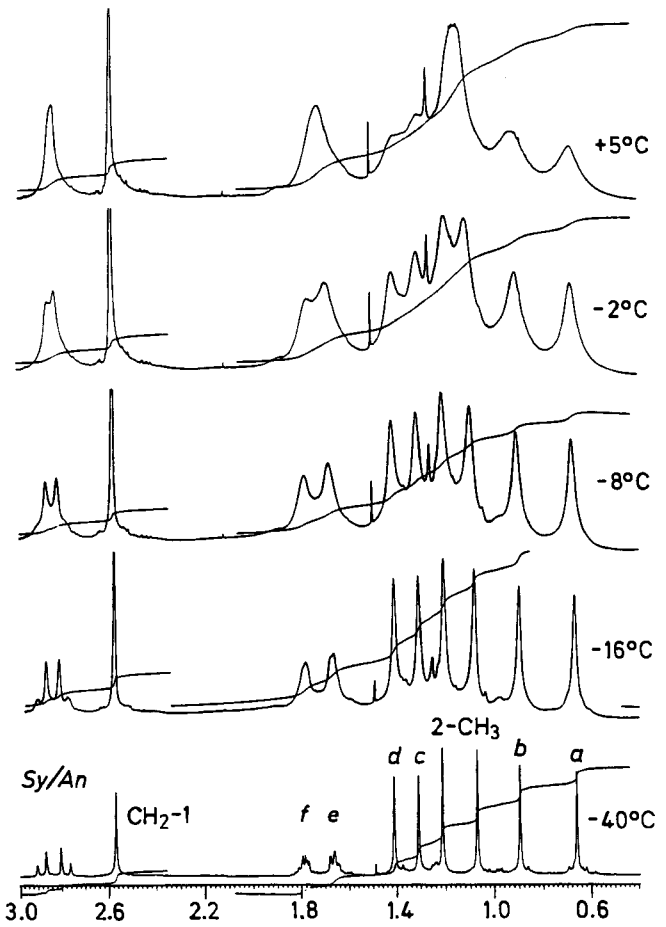
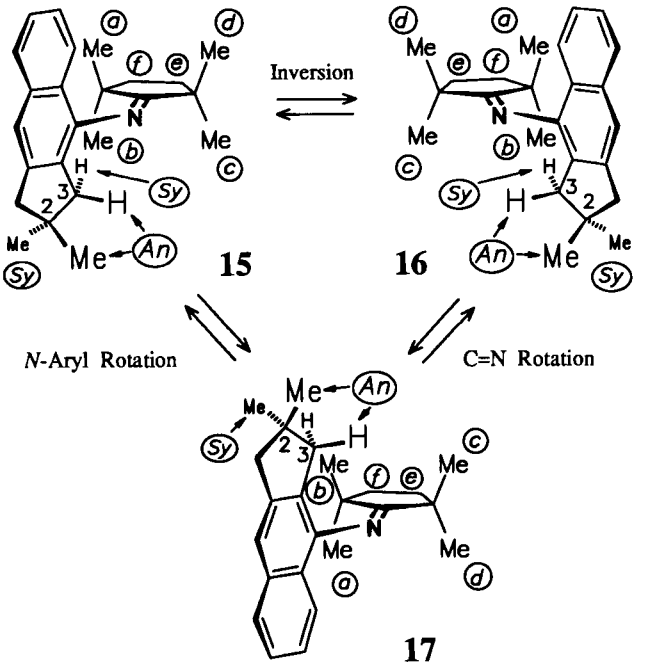


Figure 1. Temperature-dependent ^{1}H-NMR spectra (aliphatic part) of **13b** (**15**) in CD_2Cl_2 at 400 MHz (δ scale). Sharp spikes are due to contaminations and indicate good magnetic field homogeneity

are also inequivalent, and the geminal protons of at least one of the *N*-aryl methylene parts show up as an AB system (*An*/*Sy*, presumably of CH_2-3). A rather good resolution is also observed in the ^{13}C-NMR spectra (Table 1). Therefore, almost all of the reporter signals behave as designed in **8**, and the model **15** (**13b**) may be expected to perform similarly well in applications to other systems.

The onset and progress of ^{1}H-NMR coalescences with increasing temperatures are also shown in Figure 1. Saturation transfer experiments (−27°C, 80 MHz) gave independent relative assignments for the mutually exchanging signal pairs *a*/*d*, *b*/*c*, and 2-CH_3, but all absolute assignments are based only on comparisons with **13d** (see below).

The inversion process is illustrated by the formation of **16** from **15**. It results in the pairwise exchange (i) of the four octants *a*–*d*, (ii) of the cyclopentylidene sites (*e* and *f*), and (iii) of the *An* and *Sy* domains. Aryl–N single-bond rotation is exemplified by interconversion of **15** and **17**, exchanging the half-spaces *An* and *Sy* as well as different pairs of octants (*a* with *b* and *c* with *d*), but *not* the cyclopentylidene sites *e* and *f*. Because the 2-CH_3 signals are seen to exchange (Figure 1), the interconversion cannot consist of C=N rotation (**16**/**17**) alone.



Importantly, after completion of all coalescence processes above 98°C in [D_8]toluene yielding three equally intense methyl singlets (including 2-CH_3), the signal for $a = d$ remains separated from that for $b = c$ with $\Delta\delta = 0.044$ at 80 MHz in diphenyl ether up to +144°C at least, showing that aryl–N rotation requires $\Delta G^{\neq} > 23.0$ kcal/mol. Therefore, even a qualitative inspection of the *An*/*Sy* and further coalescences in Figure 1 reveals inversion (or an equivalent motion, see Section C) with time-averaged C_s symmetry.

A more stringent test is provided by rate constants for the various reporter nuclei. They were determined at variable temperatures from ^{13}C-NMR line-shape analyses (cy-

Table 1. ^{13}C-NMR chemical shifts (δ) for **12e**, **13a–f** and 1-amino-2-methylnaphthalene in $CDCl_3$

Pos. for **12e** and **13a, b**	**12e** +28°C	**13b** [a] -80°C	**13b** -43°C	**13b** +33°C	**13d** -44°C	**13d** +33°C	**13f** +32°C	**13f** [b] +108°C	**13e** -37°C	**13e** +35°C	**13e** [c] +111°C	**13c** +32°C	- [d] +28°C	Pos. for **13c - f**
2'-CH_3	-	28.26	28.3	27.1	28.2	27.4	27.4	27.2	26.2	26.5	26.6	-	-	2'-CH_3
	-	28.29	28.3	26.7	28.3	26.6	26.7	26.5	26.3	26.6	26.6	-	-	
5'-CH_3	-	25.5	25.3	26.7	24.7	26.6	26.7	26.5	-	-	-	-	-	5'-CH_3
	-	26.1	26.0	27.1	26.0	27.4	27.4	27.2	-	-	-	-	-	
C-1'	-	189.8	190.0	189.2	189.8	189.1	189.0	188.2	189.5	188.6	187.8	183.8	-	C-1'
C-2'	-	45.0	44.9	45.4	45.1	45.5	45.5	45.2	43.6	43.7	43.7	35.7	-	C-2'
C-5'	-	46.0	45.7	45.4	45.8	45.5	45.5	45.2	31.4	31.5	31.4	31.7	-	C-5'
CH_2-3'	-	35.7	35.7	37.7	35.6	37.7	37.6	37.4	39.7	40.1	40.3	24.8	-	CH_2-3'
CH_2-4'	-	38.9	38.9	37.7	38.9	37.7	37.6	37.4	20.5	20.6	20.6	24.5	-	CH_2-4'
CH_2-1	47.9	47.5	47.4	47.9	-	-	-	-	-	-	-	-	-	-
CH_2-3	44.1	45.0	44.9	45.4	18.4	18.4	18.4	18.0	17.6	17.5	17.4	17.7	17.6	2-CH_3
C-2	40.1	40.8	40.4	40.3	-	-	-	-	-	-	-	-	-	-
2-CH_3	28.8	28.4	28.6	28.8	-	-	-	-	-	-	-	-	-	-
	-	28.6	28.6	28.8	-	-	-	-	-	-	-	-	-	
C-3a	123.7	123.83	123.8	124.1	119.4	119.0	119.0	118.3	120.5	120.4	120.3	120.5	116.0	C-2
C-4	136.7	143.7	143.1	143.1	143.5	144.1	144.2	144.2	145.5	146.1	146.3	146.2	139.0	C-1
C-4a	122.6	126.8	126.7	126.4	124.7	125.0	124.9	124.6	124.8	124.8	125.2	124.9	123.2	C-8a
C-5	120.2	123.77[e]	123.4	123.5	123.6	123.9	123.9	123.6	122.4[f]	122.4[f]	122.6[f]	122.7[f]	120.2	C-8
C-6	123.6	123.81[e]	123.5	123.6	124.6	124.6	124.5	124.5	124.5[e]	124.9[e]	124.9[e]	124.9[e]	124.7	C-7
C-7	124.7	124.9[e]	124.6	124.6	124.7	124.7	124.7	124.7	125.3[e]	125.3[e]	125.2[e]	125.3[e]	124.7	C-6
C-8	128.0	127.4	127.0	127.2	127.3	127.5	127.4	127.4	127.8	127.9	127.9	127.8	128.4	C-5
C-8a	134.1	133.4	133.2	133.7	131.9	132.4	132.4	132.2	132.3	132.8	133.1	132.8	133.1	C-4a
C-9	113.6	116.7	116.8	116.7	121.7	121.7	121.6	121.3	122.1[f]	122.3[f]	122.4[f]	122.6[f]	118.1	C-4
C-9a	143.4	141.8	141.4	141.9	128.7	128.8	128.7	128.6	129.0	129.1	129.3	129.1	129.3	C-3

[a] In CD_2Cl_2. – [b] In [D_6]DMSO. – [c] In $Cl_2CD-CDCl_2$. – [d] 1-Amino-2-methylnaphthalene. – [e,f] δ values with equal labels in the same column may be interchanged.

clopentylidene C-3′/C-4′ in **13b**) and ^{1}H-NMR line-shapes (AB spectrum of CH_2-3), or at the coalescence temperatures from extrapolated signal separations in ^{1}H (2-CH_3) and ^{13}C spectra (cyclopentylidene C-2′/C-5′ and C-3′/C-4′). All rate constants of **13b** can be described by a common Arrhenius function, as shown in Figure 2; therefore, a single molecular motion should be the common cause for all of them, and its activation parameters are compiled in Table 2. Since any indication for an independent motional process was not detected, we exclude the possibility of **4** being an intermediate (rather than a transition state) which might undergo repeated aryl–N rotations during its life-time.

Pure N=C double-bond rotation would form **17** from **16** with exchange of octants but with conservation of the *An/Sy* domains. This is therefore not the observed process and hence must be much slower than inversion, as anticipated in the introduction. However, if this rotation (by +180°) were tightly coupled with an aryl–N single-bond rotation (by −180°), the combined motion would also produce the observed time-averaged C_s symmetry and thus be equivalent to inversion at nitrogen. This problem exceeds the limits of a single-compound approach and is therefore deferred to the discussion section.

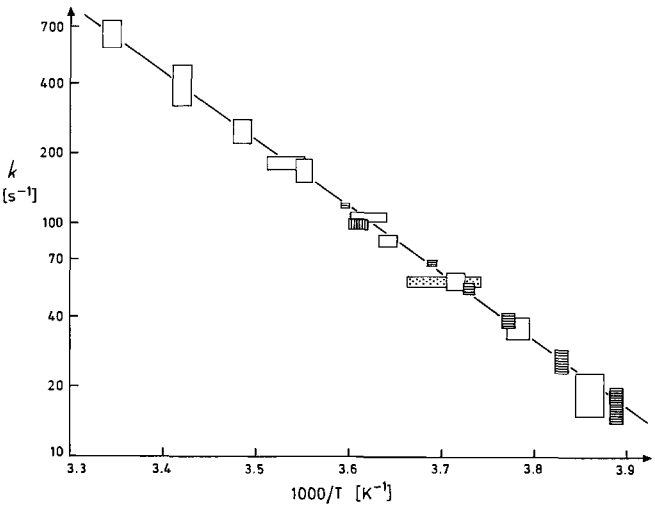


Figure 2. Arrhenius diagram for inversion at nitrogen of **13b** in CD_2Cl_2, showing the kinetic equivalence of *e/f* (open and dotted symbols) and *An/Sy* diastereotopomerizations (hatched). Open symbols for ^{13}C or ^{1}H of CH_2-3′/4′, dotted for coalescence of C-2′/5′, horizontally hatched for ^{1}H of CH_2-3, vertically hatched for ^{1}H of 2-CH_3

Table 2. Eyring parameters ΔG^{+} (kcal/mol at 298 K), ΔH^{+} (kcal/mol), and ΔS^{+} (cal mol^{-1} K^{-1}) for *anti/syn* stereomutation of sterically congested imines **13b**, **13d**, **7**, **9a**, and **9b**

No.	Solvent	ΔG^{+}	ΔH^{+}	ΔS^{+}
13b	CD_2Cl_2	13.68 (±0.02)	12.4 (±0.2)	−4 (±1)
13d	$CDCl_3$	13.65 (±0.01)	12.7 (±0.2)	−3.2 (±1)
7[15]	$CDCl_3$[a]	13.44 (±0.04)	12.8 (±0.4)	−2 (±2)
9a[17]	$CDCl_3$[a]	14.50 (±0.02)	14.0 (±0.4)	−1.7 (±2)
9b[17]	anisole	15.40 (±0.01)	15.0 (±0.4)	−1.4 (±2)

[a] Or in anisole.

The structurally simpler model **13d** without *An/Sy* substituents had been prepared in a pilot study for **13b** but turned out to be less profitable. The ^{1}H-NMR chemical shifts of its reporter nuclei for *a*–*d* are very similar to those of **13b** (as are the ^{13}C-NMR shifts in Table 1) and were assigned on the basis of NOE difference spectra[22] at −60°C in CD_2Cl_2. This was not totally unambiguous, however, under such unusual conditions and also required assignments of the aromatic protons by spectral simulation[23] (see Experimental). The NOE results could then be interpreted only with reasonable guessing[23] of the internuclear distances. Furthermore, automatic ^{1}H-NMR line-shape analyses[24] of the coalescing methyl signals of **13d** between −28 and +61°C ($CDCl_3$) were not completely satisfying[25], but they gave the activation parameters compiled in Table 2, in very good accord with the subsequent analysis of **13b**. Saturation transfer and the absence of aryl–N rotation ($\Delta G^{+} > 25.6$ kcal/mol in DMSO up to 193°C) were settled in the same way as for **13b**.

The 5-unsubstituted analogue of **13d** was observed as the single (*E*) isomer **13e**. It served as a test case of less hindered aryl–N rotation, giving $\Delta G^{+} = 18.7$ kcal/mol in $(Cl_2CD)_2$ (see Experimental). It was also used for the NMR assignments in **13b** and **13d** and for the preparation of the deuterated compound **13f**. The latter exists as a mixture of two diastereoisomers by D_6 substitution and might have shown an isotope effect on the (*E,Z*) equilibrium. This was too small to be detected, however, presumably because front strain along the N=C double bond[21] is not sufficiently large to be expressed as a steric isotope effect.

C. Discussion

The illustrations **15**–**17** provide an almost self-explanatory basis for a survey of all conceivable intramolecular motions of **13b**. By a comparison with temperature-dependent NMR spectra, the equilibration of **15** with **16** (obviously an enantiomerization) has been identified as the (*E,Z*) diastereotopomerization process. The analytical result of time-averaged C_s symmetry may be caused by a transition state with a plane of symmetry which bisects the CH_2-CH_2 bond of **13b** and contains the N=C double bond as well as the whole benz[*f*]indan skeleton. Inversion implies that the nitrogen becomes linearly coordinated; but if the C–N=C angle remains less than 180°, the inversion process might be coupled with a N=C double-bond rotation according to the elliptical movements in **5** *and* with a contrarotating motion about the aryl–N single bond. It is important to realize that these rotational moves, if occurring, must be strictly synchronized with the progressing inversion in the sense of geared motions, whereas independent N=C and aryl–N rotations have been excluded by the experimental observations.

The C–N=C angle in this or a similar transition state should be rather large, perhaps 180° as suggested by computational results mentioned in the introduction, whereas much smaller angles should cause repulsive interactions between two cyclopentylidene methyl groups (upper or lower face of **15** or **13b**) and either the *peri*-proton or the CH_2-3 group of the benz[*f*]indan moiety. Such repulsions would increase the ΔG^{+} value above that for an imine with less bulky *N*-aryl substituents, but this is not borne out by comparative data (Table 2). In the series of sterically congested imines with *N*-phenyl (**9b**), *N*-(1-naphthyl) (**9a**) and *N*-(4-benz[*f*]indanyl) (**13b**) substituents, the latter is actually the fastest according to ΔG^{+} and ΔH^{+} values and only slightly slower than **7**. Such comparisons are valid within this family since a perpendicular aryl–N conformation[21] is certainly common to all of these compounds and even maintained in the olefin[26] corresponding to **9b** (CH in place of N). Steric congestion can thus be helpful in avoiding conformational ambiguities; it has also served to avoid interfering bimolecular mechanisms[14,15] of imine stereomutation. As the electronic substituent effects[15] and the entropies of activation[14,15] are also normal in all such systems, there is no obvious experimental indication of an irregular behaviour in comparison with simpler imines. In particular, the bulky *N*-aryl substituents in our models **13b** and **d** cannot have changed the normal mechanism of imine stereomutation to any slower alternative, because the rates have been not reduced but rather increased due to steric acceleration by front strain[14,15].

An achiral transition state as discussed above is not the only possibility compatible with the time-averaged C_s symmetry. In fact, a similar but chiral transition state with the angle C–N=C <180° is a reasonable model for stereomutation in a macrocyclic bis(imine)[27]. The low[28] energetic barrier of this compound can now be explained by steric acceleration together with some angular distortion of its ground state toward the proposed transition state.

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Experimental

IR: Bruker IFS-45 and Perkin-Elmer 125. – ^{1}H-NMR: Bruker WP-80-CW, AW-80, WP-200, and Varian VXR-400S, XL-100-IL, A-60. – ^{13}C-NMR: Bruker WP-80-DS, Varian VXR-400S, XL-100-IL.

2,2-Dimethyl-1H-phenalene-1,3(2H)-dione (**10**): Obtained from the mother liquors of **12a** by further crystallization from cyclohexane; m. p. 94–97°C (ref.[29] 100–101°C; ref.[18] 83–84°C). – ^{1}H NMR (CCl_4): δ values smaller by 0.1–0.2 than in $CDCl_3$[18]. – This diketone did not rearrange[30,31] to **12a** on heating in 100% H_3PO_4 (2 h at 150°C, 23 h at 120°C) or with $AlCl_3$ in nitrobenzene (24 h at 120°C).

N,N'-Bis(2,3-dihydro-2,2-dimethyl-1H-benz[f]inden-1-ylidene)-hydrazine (**11**): A large amount of this azine may be formed in the preparation of **12b** (see below) if too much hydrazine were distilled off (above 150°C) during the initial heating period. Its constitution followed from conversion into **12b** by Wolff-Kishner reduction. The yellow needles of **11** had m. p. 185–186°C (from cyclohexane). – IR (KBr): $\tilde{\nu}$ = 1635 cm^{-1}, 1616, 752. – ^1H NMR (CCl_4): δ = 1.60 (s, $4CH_3$), 3.16 (s, $2CH_2$), 7.25 and 7.70 (AA'BB' system, 8 aromat. H), 7.61 (s, 2 4-H), 8.93 (s, 2 9-H).

$C_{30}H_{28}N_2$ (416.6) Calcd. C 86.50 H 6.78 N 6.72
Found C 86.77 H 6.96 N 6.68

2,2-Dimethyl-2H-benz[f]indene-1,3-dione (**12a**): 2,2-Dimethylmalonyl dichloride was prepared as described[18], but the presence of ca. 3 mol-% of DMF allowed the final heating period (50°C) to be shortened to 30 min; b. p. 55–58°C/21 Torr (ref.[18] 75°C/20–25 Torr; ref.[29] 45–55°C/22 Torr). This dichloride (43.0 g, 254 mmol) was added dropwise to an ice-cooled suspension of $AlCl_3$ (72.7 g, 546 mmol) in 500 ml of anhydrous CH_2Cl_2 to give a clear solution. Naphthalene (33.6 g, 262 mmol) in 125 ml of anhydrous CH_2Cl_2 was added so slowly that the internal temp. remained well below +15°C. The escaping gas (HCl) was passed onto the surface of an aqueous KOH solution. After standing at room temp. for at least 7 h the mixture was poured on ice (500 g) and extracted with CH_2Cl_2 (4 × 250 ml). The combined extracts were washed with water (300 ml), 2 N aqueous NaOH (200 ml), water (2 × 300 ml), and then dried with Na_2SO_4. The dark-coloured crystals (57.9 g, 101%) obtained by evaporation were a 58:42 mixture of **12a** and its isomer **10**. They were recrystallized twice from cyclohexane (2 × 650 ml) to give a fraction of pure **12a** (16.9 g, 30%) with m. p. 136–137°C (ref.[29] 137–137.5°C; ref.[18] 132–133°C). – ^1H NMR ($CDCl_3$): As reported in ref.[18].

2,3-Dihydro-2,2-dimethyl-1H-benz[f]indene (**12b**): A 1-l round-bottomed flask was charged with 16.9 g (75.3 mmol) of **12a**, diethylene glycol (440 ml), 100% hydrazine hydrate (63 ml, 1.3 mol), conc. hydrochloric acid (7.5 ml, 93 mmol), and a boiling-chip. A large-diameter distillation bridge (air-cooled only) was attached, and water was distilled off for 3 h at a maximal bath temp. of 140°C (see above at **11**). Solid potassium hydroxide (45.3 g, 807 mmol) was added to the cooled mixture, which was reheated to 160–170°C for 2 h and then to 190–200°C for 4 h until N_2 evolution (above 180°C) ceased. The subliming colourless needles of **12b** hat to be removed by intermittent use of an air heater. After dilution with dist. water (900 ml) and extraction with 4 batches of ether (1 l), the combined extracts were washed neutral (2 × 250 ml), dried with Na_2SO_4, and the solvent was evaporated to leave 14.4 g (97%) of pure **12b** with m. p. 100–104°C. A sample was distilled at 100–130°C/0.1 mbar and then recrystallized from methanol (17 ml/g); m. p. 102.5–105°C. – ^1H NMR (CCl_4 or $CDCl_3$): δ = 1.16 (s, $2CH_3$), 2.80 (s, $2CH_2$), 7.20 and 7.55, or 7.30 and 7.65 (AA'BB' system, 4 aromat. H), 7.41 or 7.50 (s, 4- and 9-H). – ^{13}C NMR: ($CDCl_3$): δ = 28.3 (q, $2CH_3$), 40.4 (s, C-2), 47.2 (t, C-1,3), 122.4 (d, C-4,9), 124.6 (d, C-6,7), 127.2 (d, C-5,8), 132.9 (s, C-4a,8a), 142.7 (s, C-3a,9a).

$C_{15}H_{16}$ (196.3) Calcd. C 91.78 H 8.22 Found C 92.02 H 8.25

4-Bromo-2,3-dihydro-2,2-dimethyl-1H-benz[f]indene (**12c**): A solution of 7.88 g (44.3 mmol) of *N*-bromosuccinimide (NBS) in anhydrous DMF (35 ml) was added dropwise to 8.72 g (44.4 mmol) of **12b** in 125 ml of anhydrous DMF and the mixture was stirred at room temp. for 43 h. Then it was diluted with dist. water (400 ml) and extracted with ether (5 × 100 ml). The combined extracts were thoroughly washed (at least 5 × 100 ml), dried with Na_2SO_4, and the solvent was evaporated. Distillation of the residue (12.17 g, 100%) at 115–125°C/0.03 bar gave 10.2 g (84%) of **12c** as a yellow oil. – IR (film): $\tilde{\nu}$ = 3055 cm^{-1}, 2954, 2931, 2865, 2835, 1565, 1465, 1426, 1252 (s), 765, 746. – ^1H NMR ($CDCl_3$ at 360 MHz): δ = 1.18 (s, $2CH_3$), 2.92 (2 s, $2CH_2$), 7.41 (ddd, 7-H), 7.48 (ddd, 6-H), 7.51 (s, 9-H), 7.71 (dd, 8-H), 8.16 (d, 5-H); $^3J_{56}$ = 8.5, $^3J_{67}$ = 6.8, $^3J_{78}$ = 8.4 Hz; assigned by simulation and comparison with 1-bromonaphthalene[32]. – ^{13}C NMR ($CDCl_3$): δ = 28.4 (q, $2CH_3$), 39.5 (s, C-2), 48.2 (t, C-1), 49.5 (t, C-3), 118.9 (s, C-4), 122.2 (d, C-9); 125.4, 125.9, 126.1 and 127.6 (4 d, C-5 to -8); 131.1 (s, C-4a), 134.1 (s, C-8a), 142.7 (s, C-9a), 143.5 (s, C-3a); assignments by a comparison with **12b** and naphthalenes[33].

$C_{15}H_{15}Br$ (275.2) Calcd. C 65.47 H 5.49
Found C 65.04 H 5.14

4,9-Dibromo-2,3-dihydro-2,2-dimethyl-1H-benz[f]indene was formed as a by-product by treatment of **12b** with bromine or with BrI or with more than one equivalent of NBS: Unpurified colourless solid. – ^1H NMR ($CDCl_3$ at 360 MHz): δ = 1.20 (s, $2CH_3$), 3.02 (s, $2CH_2$), 7.53 (dd, 6- and 7-H), 8.19 (dd, 5- and 8-H).

4-Amino-2,3-dihydro-2,2-dimethyl-1H-benz[f]indene (**12e**): *n*-Butyllithium (1.00 ml, 2.27 mmol) in hexane was added to a stirred solution of monobromide **12c** (607 mg, 2.21 mmol) in 2 ml of anhydrous ether at –75°C under Ar. This yellow solution of **12d** was stirred for 2 h up to room temp. and added within 10 min by means of a syringe to a stirred solution of 575 mg (2.09 mmol) of diphenylphosphoryl azide[20] ($C_{12}H_{10}N_3O_3P$) in anhydrous ether (20 ml) at –75°C. The resulting suspension was stirred at –50 to –20°C for 2 h and recooled to –70°C before the addition of $LiAlH_4$ (280 mg, 7.4 mmol). During warm-up in an efficient hood, reduction started above –10°C (N_2 evolution) and was accompanied by an awful smell from phosphanes. After at least 3 h at room temp. the residual alanate was destroyed by slow addition of ethyl acetate (2.5 ml), then methanol (5 ml) and water (3 ml). The mixture was diluted with more ether and washed with 2 N aqueous NaOH. After extraction of **12e** into 6 N HCl (3 × 20 ml), the ethereal phase was washed and dried to give 175 mg (40%) of the hydrocarbon **12c**. The combined acidic extracts were made alkaline and shaken with CH_2Cl_2 (3 × 20 ml), which was then washed neutral, dried with Na_2SO_4, and concentrated to yield 260 mg (59%) of clean **12e**. Further purification of this air-sensitive amine was not successful by distillation at 110–160°C (bath temp.)/0.001 mbar. The colourless oil **12e** (232 mg, 52%) transformed slowly into a waxy solid with m. p. 55–65°C. – IR (KBr): $\tilde{\nu}$ = 3371 and 3235 cm^{-1} (NH_2), 3065, 2953, 2866, 1637, 1620, 1429, 741. – ^1H NMR (CCl_4): δ = 1.18 (s, $2CH_3$), 2.61 (s, CH_2-3), 2.80 (s, CH_2-1), 4.15 (s, NH_2), 6.97 (s, 9-H), 7.19 and 7.55 (2 mc, 5- to 8-H). – ^{13}C NMR ($CDCl_3$): Table 1, assignment by a comparison with naphthalenes[33].

All used equipment must be cleaned with $KMnO_4$ solution for removal of the malodorous contaminations. These are also formed with the originally applied mixed hydride[20] which reacts rather slowly. The amination of **12d** with tosyl azide and $LiAlH_4$ is possible and may diminish the stench problems.

2,3-Dihydro-2,2-dimethyl-4-[(2,2,5,5-tetramethylcyclopentylidene)amino]-1H-benz[f]indene (**13b**): The amine **12e** (990 mg, 4.69 mmol), cyclopentanone diethyl acetal[34] (1.50 g, 9.5 mmol), and 25 mg of anhydrous $ZnCl_2$ were slowly heated from 100 to 140°C (4.5 h) for distillation of nascent ethanol. Unreacted acetal was removed at 140°C/11 Torr to leave 1.49 g of crude **13a** which was sensitive to hydrolysis and could not be purified. – ^1H NMR (CCl_4): δ = 1.16 (s, $2CH_3$), 1.80 and 2.50 (2 mc, CH_2 and contaminations), 2.80 (s, CH_2-1), 7.18 (s and m, 3H), 7.49 (m, 2H).

This crude imine (**13a**, assumed 4.69 mmol) was exhaustively permethylated according to the general procedure of ref.[14] Work-

up without acidification[14] left 1.33 g (85%) of brown oil **13b** not contaminated by **13a**. It was distilled at 180–210°C (bath temp.)/0.01 mbar to give a solidifying yellow oil (590 mg, 38%). – IR (KBr): $\tilde{\nu}$ = 3062 cm^{-1}, 2955, 2866, 1683, 1574, 1460, 1364, 1036, 746.

$C_{24}H_{31}N$ (333.5) Calcd. C 86.43 H 9.37 N 4.20
Found C 85.88 H 9.75 N 4.05

A completely pure sample was obtained by treatment of 60 mg of the hydrogen perchlorate **14b** (see below) with 2 N aqueous NaOH and extraction with CH_2Cl_2: ^1H NMR (CD_2Cl_2 at −30°C): δ = 0.66 (s, 5′-CH_3, *a*), 0.89 (s, 5′-CH_3, *b*), 1.07 (s, 2-CH_3, *Sy*), 1.21 (s, 2-CH_3, *An*), 1.31 (s, 2′-CH_3, *c*), 1.41 (s, 2′-CH_3, *d*), 1.66 and 1.78 (AA′BB′ system, CH_2-3′ and -4′, *e/f*), 2.57 (s, CH_2-1), 2.776 and 2.878 (AB system, ^2J = 15.5 Hz, *Sy* and *An*), 7.28 (dd, ^4J = 1.3, ^3J = 7.5 Hz, 6-H), 7.29 (s, 9-H), 7.35 (dd, ^4J = 1.2, ^3J = 7.5 Hz, 7-H), 7.49 (dd, ^3J = 8.2 Hz, 8-H), 7.69 (d, ^3J = 8 Hz, 5-H); assigned by a comparison with **13d**. – Saturation transfer (−27°C, intensity −40%): δ = 0.66/1.41 (*a/d*), 0.89/1.31 (*b/c*), and 1.07/1.21 (*Sy/An*). – Temperature dependence of chemical shifts (−105 to +5°C) in line-shape analyses: +0.0005 ppm/K (2-CH_3, *Sy*), −0.0003 ppm/K (2-CH_3, *An*), +0.00013 ppm/K (3-H, *Sy*), −0.000185 ppm/K (3-H, *An*). – ^{13}C NMR: Table 1, assignment by a comparison with **13d**, temperature dependence less than ±0.3 ppm between −80 and +37°C in CD_2Cl_2, except for C-1′ (−1 ppm), CH_2-1 (+0.6), CH_2-3 (+0.7), and C-2 (−0.5); coalescences (25.16 MHz): CH_2-3′/4′ at +10 (±2)°C with Δδ = 3.29, C-2′/5′ at −3 (±3)°C with Δδ = 1.02, 2-CH_3 (*An/Sy*), and 2′,5′-CH_3.

1-Amino-2-methylnaphthalene: Obtained in 92–95% yield by hydrogenation[35,36] of commercial 2-methyl-1-nitronaphthalene. – ^1H NMR (CCl_4): δ = 2.14 (s, CH_3), 3.70 (br s, NH_2), 7.06 (s, 2H), 7.25 (mc, 2H), 7.56 (mc, 2H). – ^{13}C NMR: Table 1; cf. ref.[37] (in [D_6]acetone). – This air-sensitive amine may be stored for longer periods as the hydrochloride[36].

1-[(Cyclopentylidene)amino]-2-methylnaphthalene (**13c**): 1-Amino-2-methylnaphthalene (3.47 g, 22.1 mmol) was treated as described for **13b** (via **13a** from **12e**) but with heating to 190°C for 1 h. The pale yellow oil (3.30 g, 67%) distilled at 125–140°C (bath temp.)/0.07 mbar. – IR (film): $\tilde{\nu}$ = 3050 cm^{-1}, 2960, 2870, 1680, 1373, 803. – UV (cyclohexane): λ_{max} (lg ε) = 267 nm (3.635), 291 (sh, 3.720), 301 (3.743), 314 (3.638), 329 (3.501). – ^1H NMR (CCl_4): δ = 1.78 (mc, 6 H), 2.13 (s, CH_3), 2.62 (t, ^3J = 7 Hz, CH_2-2), 7.23 (mc, 4 H), 7.60 (mc, 2 H). – ^{13}C NMR: Table 1.

$C_{16}H_{17}N$ (223.3) Calcd. C 86.06 H 7.67 N 6.27
Found C 86.41 H 7.87 N 6.08

2-Methyl-1-[(2,2,5,5-tetramethylcyclopentylidene)amino]naphthalene (**13d**): Imine **13c** (3.30 g, 14.2 mmol) was exhaustively permethylated according to the general procedure[14]. Distillation at 112–138°C/0.01 mbar afforded 3.63 g (91%) of pure **13d** as a yellow, very viscous oil. – IR (film): $\tilde{\nu}$ = 3048 cm^{-1}, 2955, 2870, 1682, 1460, 1370, 801. – UV (Cyclohexane): λ_{max} (lg ε) = 307 nm (3.775), 320 (sh, 3.738), 333 (sh, 3.613). – ^1H NMR (CCl_4 at 60 MHz and +29°C): δ = 1.01 (br s, 2 CH_3, sharp at +75°C), 1.07 (s, 2 CH_3), 1.64 (s, 2 CH_2), 2.12 (s, *o*-CH_3), 7.15 (mc, 4 H), 7.46 (m, 2 H). – ^1H NMR ($CDCl_3$ at 60, 90, and 200 MHz), computer simulation[23] of the aromatic part: δ = 7.268(7) (4-H), 7.379(8) (6-H), 7.386(7) (7-H), 7.455(6) (3-H), 7.613(4) (8-H), 7.761(3) (5-H), assignments by means of NOED spectra[22] and a comparison with 1-(dimethylamino)naphthalene[38]; coupling constants (Hz): 8.61(4) (3,4-H), 8.73(8) (5,6-H), 0.93(8) (5,7-H), 0.56(3) (5,8-H), 6.92(3) (6,7-H), 1.39(9) (6,8-H), 8.19(7) (7,8-H). – Temperature dependence of chemical shifts in line-shape analyses[23] (100 MHz in $CDCl_3$): −0.00016 ppm/K (5′-CH_3, *a*), −0.00036 ppm/K (5′-CH_3, *b*), −0.00026 ppm/K (2′-CH_3, *c*), − 0.00026 ppm/K (2′−CH_3, *d*). – Saturation transfer ($CHCl_3$, −27°C, 100 MHz, intensity −30%): δ = 0.57/1.36 (*a/d*) and 0.79/1.27 (*b/c*). – ^1H NMR (DMSO at +193°C): δ = 0.98 and 1.05 (2 s, 2 × 2 CH_3), 1.73 (s, 2 CH_2). – ^{13}C NMR: Table 1; assignment by a comparison with compound **16** reported in ref.[39]

$C_{20}H_{25}N$ (279.4) Calcd. C 85.97 H 9.02 N 5.01
Found C 85.82 H 9.15 N 5.01

1-[(2,2-Dimethylcyclopentylidene)amino]-2-methylnaphthalene (**13e**): Titanium tetrachloride (2.30 ml, 21 mmol) in 10 ml of anhydrous toluene was added dropwise to a stirred solution of 2,2-dimethylcyclopentanone[39] (3.40 g, 30.4 mmol) and 1-amino-2-methylnaphthalene (15.7 g, 100 mmol) in 40 ml of anhydrous toluene. After 7 h of refluxing at 130°C, the precipitate was digested with ether (4 × 50 ml) and separated by suction. The dried extracts left 7.20 g of a crude oil which was purified as the salt **14e** (see below). The free base **13e** (2.60 g, 34%) was recovered by shaking with 2 N aqueous NaOH/ether and distilled at 150–165°C (bath temp.)/0.4 Torr as a yellow oil. – IR (film): $\tilde{\nu}$ = 3050 cm^{-1}, 2958, 2870, 1680, 1373, 806. – UV (cyclohexane): λ_{max} (lg ε) = 302 nm (3.759), 313 (3.701), 328 (3.572). – ^1H NMR (CCl_4): δ = 1.32 and 1.41 (2 s, 2 2′-CH_3, Δν = 5.8 Hz, coalesced at +85°C), 1.73 (m, 3 CH_2), 2.12 (s, *o*-CH_3), 7.26 (mc, 4 H), 7.65 (mc, 2 H). – ^{13}C NMR ($Cl_2CD-CDCl_2$ at +35°C): As in $CDCl_3$ (+35°C, Table 1) within 0.2 ppm, assigned by a comparison with compound **14** reported in ref.[39]; CH_2-5′ exchangeable with [OD]methanol to give a t with $^1J_{CD}$ = 20 Hz and isotope shift $^2\Delta$ = −0.1 ppm (upfield) on CH_2-4′; coupling constants $^1J_{CH}$ (Hz) = 126 (q, 2′-CH_3), 129 (t, CH_2-3′), 132 (t, CH_2-4′), 126 (q, *o*-CH_3). – Coalescence of 2′-CH_3 at +60 (±5)°C (60 MHz), Δν = 1.8 Hz constant between −37 and +53°C, $\Delta G^{\neq}$ = 18.6(3) kcal/mol.

$C_{18}H_{21}N$ (251.4) Calcd. C 86.01 H 8.42 N 5.57
Found C 86.05 H 8.44 N 5.74

1-{[2,2-Bis(trideuteriomethyl)-5,5-dimethylcyclopentylidene]amino}-2-methylnaphthalene (**13f**): The 2,2-dimethyl imine **13e** (0.75 g, 3 mmol) was exhaustively alkylated with CD_3I according to the general procedure[14]. The product (0.43 g, 50%) was isolated as described for its unlabelled analogue **13d**. – ^1H NMR ($CDCl_3$ at −37°C): δ = 0.63 and 0.87 (2 s, 2 × 5′-CH_3, intensity 3.0 ± 0.1), 1.38 and 1.48 (2 s, 2 × 2′-CH_3), 1.73 (m, CH_2-3′ and -4′), 2.23 (s, *o*-CH_3), rest as for **13d**. – ^{13}C NMR ($CDCl_3$ at −42°C): As for **13d** at −44°C (Table 1) within 0.15 ppm, and isotope shifts $^2\Delta$ = −0.42 ppm (upfield, C-2′ and C-5′), $^3\Delta$ = −0.13 (CH_2-3′,4′).

(2,3-Dihydro-2,2-dimethyl-1H-benz[f]inden-4-yl)(2,2,5,5-tetramethylcyclopentylidene)ammonium Perchlorate (**14b**): A solution of distilled imine **13b** (463 mg, 1.39 mmol) in ether (15 ml) was precipitated with 0.12 ml of $HClO_4$ (70%). The salt was washed with ether (4 × 5 ml) and recrystallized from 3 ml of 2-propanol. A first crop (20 h at +4°C) had m.p. 205–220°C (dec.); total yield 177 mg (29%) of an almost colourless powder by very slow crystallization. – ^1H NMR ($CDCl_3$ at +32°C): δ = 0.85 and 1.02 (2 s, 2 × 5′-CH_3), 1.19 (s, 2 × 2-CH_3), 1.71 and 1.80 (2 s, 2 × 2′-CH_3), 1.96 (pseudo-s, CH_2-3′ and -4′), 2.90 (s, CH_2-1), 2.55 and 3.08 (AB system, ^2J = 16 Hz, CH_2-3), 7.40 (mc, 6-, 7-, and 9-H), 7.70 (m, 5- and 8-H), 12.6 (br s, NH): assigned by a comparison with compounds **5** reported in ref.[14]

$C_{25}H_{32}ClNO_4$ (434.0) Calcd. C 66.42 H 7.43 N 3.23
Found C 66.58 H 7.56 N 3.11

(2,2-Dimethylcyclopentylidene)(2-methyl-1-naphthyl)ammonium Tetrafluoroborate (**14e**): The crude imine **13e** (maximum content 30.4 mmol) required 12.5 ml (88 mmol) of aqueous HBF_4 for precipitation on cooling in ice. After isolation by suction (8.20 g, 79%),

drying in vacuo, and recrystallization from 40 ml of 1-butanol, the colourless salt (3.80 g, 37%) had m.p. 198–199°C. – IR (KBr): $\tilde{\nu}$ = 2480 cm^{-1} (v br), 1674, 1124, 1086. – ^1H NMR ($CDCl_3$): δ = 1.63 and 1.72 (2 s, 2 × 2′-CH_3), 2.37 (s, o-CH_3), rest not assigned.

$C_{18}H_{22}BF_4N$ (339.2) Calcd. C 63.74 H 6.54 N 4.13
Found C 64.06 H 6.18 N 4.19

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* Dedicated to Professor *Heinrich Nöth* on the occasion of his 65th birthday.

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