

Empirical Substituent Parameters for *E/Z* Equilibrium Constants¹⁾

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A set of substituent parameters λ^d is proposed which permits the prediction of *E/Z* equilibrium constants for olefins, enamines, Schiff bases, hydrazones, semicarbazones, oximes, and nitrones. The set includes values for the „non-bonded“ electron pairs and the nitrone oxygen as well as for amino or phenyl groups coplanar and orthogonal to the double bond. Ketone anils prefer a perpendicular phenyl group. Principal limitations of the very simple heuristic model are discussed. The model is also applied to the „*cis*“- and „*ortho*“-effects, enolates, and Schiff bases of cyclic and bicyclic ketones.

Empirische Substituentenparameter für *E/Z*-Gleichgewichtskonstanten¹⁾

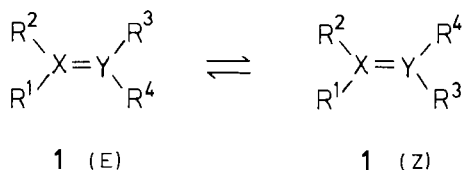
Ein vorgeschlagener Satz von Substituentenparametern λ^d erlaubt die Vorhersage der *E/Z*-Gleichgewichtskonstanten bei Olefinen, Enaminen, Schiffischen Basen, Hydrazonen, Semicarbazonen, Oximen und Nitronen. Der Parametersatz enthält Werte für „nichtbindende“ Elektronenpaare und Nitronsauerstoff sowie für Amino- und Phenylgruppen, die koplanar oder orthogonal zur Doppelbindung gestellt sind. Phenylreste in Ketonanilen bevorzugen die Orthogonalkonformation. Grundsätzliche Beschränkungen des sehr einfachen heuristischen Modells werden besprochen. Es läßt sich anwenden auf den „*cis*“- und den „*ortho*“-Effekt, auf Enolate und Schiffische Basen cyclischer und bicyclischer Ketone.

E/Z isomerism²⁾ of compounds **1** with various kinds of double (or partially double) bonds has frequently been studied by NMR spectroscopy. A systematic rationalization and hence interpretation of such a wealth of data could be valuable in predicting *E/Z* equilibrium ratios. Inspired by an apparently undeveloped early idea due to Ruch and Ugi³⁾, I propose to utilize a very simple approach by which such equilibria can be calculated from a tentative set of substituent parameters λ^d and sensitivity factors ρ^d .

Although the model to be described below does not involve chirality, it is formally akin to chirality functions^{3,4)} which were occasionally used for quantitative descriptions of asymmetric induction^{4,5)}, conformational equilibria⁶⁾, and optical rotations⁷⁾.

A. Procedure and Results

Notations for the *E*- and *Z*-isomers²⁾ of **1** are obtained by ordering the substituents R^i according to the priority⁸⁾ sequence ($R^2 > R^1$ and $R^4 > R^3$ within each pair). The basic assumption is³⁾ that the natural logarithm of the *E/Z* concentration ratio at thermal equilibrium may be calculated from eq. (1); i.e., from the product of differences of substituent parameters at double bonds, $\lambda^d(R)$.



class names	XY	special R ⁱ	ρ _{XY}
olefins, enamines	CC	—	0.95
imines, hydrazones, oximes	CN	R ³ = n	3.1
nitrones	CN ⁺	R ⁴ = O [⊖]	5 (±1)

Table 1. Parameters λ^d(R) for substituents R in 1, ordered by increasing priority (n = non-bonded electron pair)

R	λ ^d (R)	R	λ ^d (R)
n	-0.6	C ₆ H ₅ ⊥ ^{c)}	0.6
H	0	C ₆ H ₄ CH ₃ -(2)	0.8
CH ₂ [⊖]	ca. 0	2-naphthyl	1.6
CH ₃	1	1-naphthyl	0.8
C ₂ H ₅	1.38	C ₆ H ₃ (CH ₃) ₂ -(2,6)	0.55
n-C ₃ H ₇	1.41	C ₆ H ₃ (CH ₃) ₃ -(2,4,6)	0.45
n-C ₄ H ₉	1.41	C ₆ H ₂ (CH ₃) ₄ -(2,3,5,6)	0.32
n-C ₅ H ₁₁	1.41	C ₆ (CH ₃) ₅	0.30
CH ₂ CH(CH ₃) ₂	1.4	9-anthryl	0.41
CH ₂ C(CH ₃) ₃	1.41	CO ₂ R	ca. 2.5
CH ₂ C ₆ H ₅	1.25	CHCl ₂	1.6
CH(CH ₃) ₂	1.58	NHR	0.9
s-C ₄ H ₉	1.55	N(CH ₃) ₂ ^{c)}	0.8
c-C ₃ H ₅	1.45	N(CH ₃)C ₆ H ₅ ^{c)}	1.1
c-C ₆ H ₁₁	1.45	NRR' ^{a)}	3.0
CH(C ₆ H ₅) ₂	1.5	O [⊖]	0.0
t-C ₄ H ₉	ca. 3	OR	0.5
C ₆ H ₅ ^{a)}	3.0	Cl	ca. 1.3
C ₆ H ₅ ^{b)}	1.6	Br	ca. 1.6

a) Substituent coplanar to the double bond. — b) Phenyl with neighbouring n-alkyl substituent. — c) Substituent perpendicular to the double bond.

$$\ln K = \ln \frac{[E]}{[Z]} = \rho_{XY} [\lambda^d(R^1) - \lambda^d(R^2)] [\lambda^d(R^3) - \lambda^d(R^4)] \quad (1)$$

The sensitivity factors ρ_{XY} of eq. (1) derived in this work are shown below formulae 1 for three classes of compounds. Very often the Z-isomer is disfavoured with negative ΔG° for Z → E transformation, or positive ln K = -ΔG°/RT. Eq. (1) obviously constitutes a linear free energy relationship with permutation properties appropriate for E/Z equilibria. If the substituents at one end of the double bond were interchanged, the sign inversion in eq. (1) would correspond to calculating the ratio [Z]/[E], or 1/K;

if the interchange is performed at each end, no sign inversion occurs. It is therefore sufficient to write down solely the *E*-isomer and then to transfer the substituent parameters $\lambda^d(\text{R})$ to eq. (1) in cyclic sequence according to **1-(E)**.

Since eq. (1) contains only parameter differences, the origin may be chosen arbitrarily for hydrogen, setting $\lambda^d(\text{H}) = 0$. Furthermore, multiplying all parameters by a constant factor *c* is equivalent to multiplying the sensitivity factor by c^2 . Therefore, one has to define one further parameter to fix the total scale. I chose to define $\lambda^d(\text{CH}_3) = 1$ as was originally suggested for chirality functions³⁾. The remaining parameters $\lambda^d(\text{R})$ are shown in table 1 and will be derived and discussed in the subsequent sections.

Substituent specifications, $\ln K$, and experimental %*E* values have been collected in Tables 2–5 from literature references^{9–61)} for olefins (entries 1–22), enamines (entries 23–48), Schiff bases (entries 49–139), hydrazones, semicarbazones, and oximes with oxime ethers (entries 140–195), and nitrones (entries 196–203), together with %*E* values as calculated *via* eq. (1). For convenience and easy location, the compounds within each table were arranged in the order of minimal priority⁸⁾ for $\text{R}^1 - \text{R}^4$ in sequence.

Primary Data

Experimental data taken from various literature references appeared to be of quite diverse quality. An overall optimization procedure⁶⁾ thus should include appropriate weight factors which are quite difficult to estimate. Therefore, I adopted a rather simple-minded approach, assigning primary significance to some substituent parameters derived from sets of data which belonged to sufficiently extended series or fell among those of relatively high precision. Following the evaluation of sensitivity factors ρ_{XY}^d , the rest of substituent parameters was computed, including those of lower reliability. Examples of this procedure will now be described.

The choice of $\lambda^d(\text{CH}_3) - \lambda^d(\text{H}) = 1$ renders the determination of the olefin sensitivity factor rather trivial. From equilibration studies during the metathesis reaction of 2-butene (entry 1a in table 2) one obtains $\rho_{\text{CC}} = +0.95$ with eq. (1). Hence λ^d values for ethyl (entry 2) and isopropyl substituents (entry 6) as well as for *n*-alkyl groups (average from entries 3–5 and 11–13) and coplanar phenyl (entry 8) can be computed.

It is possible to examine the transferability of these parameters to CN double bond systems without knowledge of ρ_{CN} . Differences of experimental $\ln K$ values were computed according to the left-hand side of eq. (2); the combination of two such $\Delta \ln K$ for any fixed specifications X, Y, R^2 , R^3 , and R^4 gives the linear eq. (3). Plots of $\Delta \ln K$ pairs against each other showed good linearity and, independently of $\text{R}^2 - \text{R}^4$, the expected positive slope which was common for all eight points with $\text{R}^1 = \text{CH}(\text{CH}_3)_2$ at an olefinic position as well as at the carbon or nitrogen sites of CN double bonds or at nitrones. Therefore, λ^d for isopropyl is valid at any such position. In a similar way, λ^d was determined for benzyl as R^1 .

$$\ln K \left(\begin{array}{c} \text{R}^2 \\ \diagdown \\ \text{X} = \text{Y} \\ \diagup \\ \text{R}^1 \end{array} \begin{array}{c} \text{R}^3 \\ \diagup \\ \text{R}^4 \end{array} \right) - \ln K \left(\begin{array}{c} \text{R}^2 \\ \diagdown \\ \text{H}_3\text{C} \\ \diagup \\ \text{R}^4 \end{array} \begin{array}{c} \text{R}^3 \\ \diagup \\ \text{R}^4 \end{array} \right)$$

$$= \Delta \ln K(\text{R}^1, \text{CH}_3) = \rho_{\text{XY}}[\lambda^d(\text{R}^1) - \lambda^d(\text{CH}_3)][\lambda^d(\text{R}^3) - \lambda^d(\text{R}^4)] \quad (2)$$

$$\Delta \ln K(\text{R}^1, \text{CH}_3) = \Delta \ln K(\text{C}_2\text{H}_5, \text{CH}_3) \frac{\lambda^d(\text{R}^1) - \lambda^d(\text{CH}_3)}{\lambda^d(\text{C}_2\text{H}_5) - \lambda^d(\text{CH}_3)} \quad (3)$$

With this background, the product in eq. (4), where n is the non-bonded electron pair, can be deduced from a series of compounds with common $R^4 = \text{CH}_3$ according to eq. (5):

$$\rho_{\text{CN}}[\lambda^d(\text{CH}_3) - \lambda^d(n)] = 5 (\pm 0.2) \quad (4)$$

$$\begin{aligned} & \ln K \left(\begin{array}{c} R^{2a} \\ \diagup \\ \text{C}=\text{N} \\ \diagdown \\ R^1 \end{array} \text{---} \text{CH}_3 \right) - \ln K \left(\begin{array}{c} R^{2b} \\ \diagup \\ \text{C}=\text{N} \\ \diagdown \\ R^1 \end{array} \text{---} \text{CH}_3 \right) \\ &= \Delta \ln K(R^{2b}, R^{2a}) = \rho_{\text{CN}}[\lambda^d(\text{CH}_3) - \lambda^d(n)][\lambda^d(R^{2a}) - \lambda^d(R^{2b})] \end{aligned} \quad (5)$$

While this product is thus obtained with good precision independently of R^1 and R^2 , its factors may be evaluated less precisely but independently as follows.

$$\begin{aligned} & \ln K \left(\begin{array}{c} R^2 \\ \diagup \\ \text{C}=\text{N} \\ \diagdown \\ R^1 \end{array} \text{---} R^{4a} \right) : \ln K \left(\begin{array}{c} R^2 \\ \diagup \\ \text{C}=\text{N} \\ \diagdown \\ R^1 \end{array} \text{---} R^{4b} \right) \\ &= \frac{\lambda^d(R^{4a}) - \lambda^d(n)}{\lambda^d(R^{4b}) - \lambda^d(n)} \end{aligned} \quad (6)$$

The quotient in eq. (6) of experimental $\ln K$ values was found to be independent of R^1 and R^2 ; thus the right-hand side could be solved for $\lambda^d(n) = -0.6 (\pm 0.2)$ with known parameters for R^{4a} and R^{4b} .

On the other hand, $\lambda^d(9\text{-anthryl}) = +0.41$ can be calculated with eq. (4) from entries 62b and 105 directly. Substituting this value for R^2 in eq (7) and using known R^4 values (entries 62–64 and 66), one obtains $\rho_{\text{CN}} = 3.1 (\pm 0.2)$.

$$\ln K \left(\begin{array}{c} R^2 \\ \diagup \\ \text{C}=\text{N} \\ \diagdown \\ \text{H} \end{array} \text{---} R^4 \right) - \ln K \left(\begin{array}{c} R^2 \\ \diagup \\ \text{C}=\text{N} \\ \diagdown \\ \text{H} \end{array} \text{---} \text{CH}_3 \right) = \rho_{\text{CN}} \lambda^d(R^2)[\lambda^d(R^4) - \lambda^d(\text{CH}_3)] \quad (7)$$

Secondary Data

By similar techniques, it is possible to compute $\rho_{\text{CN}^+} = 5 (\pm 1)$ as the sensitivity factor for the nitrones of table 5 and $\lambda^d(\text{O}^\ominus) = 0 (\pm 0.1)$. Further substituent parameters $\lambda^d(R^2)$ may then generally be determined as the slopes of plots according to eq. (8) for various known values of R^1 , R^3 , R^4 , and ρ_{XY} .

$$\ln K(1) + \rho_{\text{XY}} \lambda^d(R^1)[\lambda^d(R^4) - \lambda^d(R^3)] = \lambda^d(R^2) \rho_{\text{XY}} [\lambda^d(R^4) - \lambda^d(R^3)] \quad (8)$$

For computational reasons, the precision given in Table 1 is often higher than warranted by the accuracy and paucity of experimental data. Some additional parameters are being derived in section D.

B. Discussion

Inspection of Tables 2–5 shows that the agreement between experimental and calculated E concentrations is generally much better than might be expected for the simple model expressed in eq. (1). In judging the accuracy of experimental data, one must be aware of several complications. For some olefins, only the difference of heats of formation is known whereas eq. (1) refers to ΔG° . As in the case of equilibria reported at temperatures other than ambient, then assumptions have to be made about the entropy. Chemical equilibration (e. g., by olefin metathesis or carbanionic intermediates) is

Table 2. Experimental and calculated *E/Z* equilibria of some olefins and enamines 1
(X = Y = C)

Entry	R ¹	R ²	R ³	R ⁴	lnK	lit. ref.	% <i>E</i> exp.	% <i>E</i> calc.
1a	H	CH ₃	H	CH ₃	0.94	9)	72	a)
1b	H	CH ₃	H	CH ₃	1.05	10,11)	74	72
2	H	CH ₃	H	C ₂ H ₅	1.32	9,10)	79	a)
3	H	CH ₃	H	n-C ₃ H ₇	1.45	9)	81	79
4	H	CH ₃	H	n-C ₄ H ₉	1.33	9)	79	79
5	H	CH ₃	H	n-C ₅ H ₁₁	1.33	9)	79	79
6	H	CH ₃	H	i-C ₃ H ₇	b)	12)	82	a)
7	H	CH ₃	H	t-C ₄ H ₉	b)	12)	>99.92	95
8	H	CH ₃	H	C ₆ H ₅	2.77	13)	96	95
9	H	CH ₃	CH ₃	C ₆ H ₅	1.31	14,15)	79 ^{c)}	64
10	H	C ₂ H ₅	H	C ₂ H ₅	1.82	9,11)	86	86
11	H	n-C ₃ H ₇	H	n-C ₃ H ₇	1.59	9)	83	87
12	H	n-C ₄ H ₉	H	n-C ₄ H ₉	1.52	9)	82	87
13	H	n-C ₅ H ₁₁	H	n-C ₅ H ₁₁	1.59	9)	83	87
14	H	[CH ₂] ₇ CH ₃	H	[CH ₂] ₇ CO ₂ CH ₃	1.39	16)	80	79
15	H	CH ₂ C ₆ H ₄ R-(4)	H	C ₆ H ₄ R-(4)	3.9	17)	98 ^{d)}	97
16a	H	CH ₂ C ₆ H ₅	CH ₃	C ₆ H ₅	1.24	15)	78	67
16b	H	CH ₂ C ₆ H ₅	CH ₃	C ₆ H ₅	1.14	15)	76 ^{c)}	67
17	H	CH(CH ₃)C ₆ H ₅	H	C ₆ H ₅	3.5	15)	97	99
18	H	t-C ₄ H ₉	H	t-C ₄ H ₉	b)	12)	>99.99	99.98
19	H	C ₆ H ₅	H	C ₆ H ₅	b)	18)	>99.99	99.99
20	H	C ₆ H ₅	H	CO ₂ CH ₃	b)	18)	>99.88	99.93
21	H	C ₆ H ₅	CH ₃	C ₆ H ₅	1.10	19)	75	85
22	H	CO ₂ C ₂ H ₅	H	CO ₂ C ₂ H ₅	b)	18)	>99.91	99.7
23	H	CH ₃	H	NR ₂	>3	20)	>95	95
24	H	CH ₃	C ₂ H ₅	N(C ₂ H ₅) ₂	1.82	21)	86	82
25	H	CH ₃	c-C ₃ H ₅	N(C ₂ H ₅) ₂	0.85	22)	70	81
26	H	CH ₃	C ₆ H ₅	N(C ₂ H ₅) ₂	2.20	21)	90	91
27	H	CH ₃	C ₆ H ₅	N(CH ₂) ₅	2.94	21)	95	91
28	H	CH ₃	C ₆ H ₅	N(CH ₂ CH ₂) ₂ O	3.89	21)	98	91
29	H	C ₂ H ₅	H	N(CH ₂ CH ₂) ₂ O	>3.9	23)	>98	98
30	H	CH ₂ CH ₂ NR ₂	c-C ₃ H ₅	N(C ₂ H ₅) ₂	2.94	22)	95	89
31	H	CH ₂ CH ₂ NR ₂	c-C ₃ H ₅	NR ₂	>3	22)	>95	89
32	H	CH ₂ C ₆ H ₅	H	N(CH ₃) ₂	>3.2	24)	>96	97
33	H	C ₆ H ₅	H	N(CH ₂ CH ₂) ₂ O	>4.6	23)	>99	99.98
34	H	C ₆ H ₅	CH ₃	N(CH ₂ CH ₂) ₂ O	3.48	21)	97	95
35	H	C ₆ H ₅	CH ₂ C ₆ H ₅	N(CH ₂ CH ₂) ₂ O	2.94	21)	95	93
36	H	C ₆ H ₅	C ₆ H ₅	N(CH ₂ CH ₂) ₂ O	1.99	21,25)	88	97
37	H	CO ₂ CH ₃	H	NR ₂	>3.9	26)	>98	99.92
38	H	CO ₂ CH ₃	CO ₂ CH ₃	NR ₂	>3.9	26)	>98	>98
39	H	N(CH ₃) ₂	aryl	N(CH ₃) ₂	0.20	23)	55	64
40	CH ₃	C ₆ H ₅	H	N(CH ₂) ₄	1.39	21)	80	85
41	CH ₃	C ₆ H ₅	H	N(CH ₂) ₅	1.99	21)	88	85
42	CH ₃	C ₆ H ₅	H	N(CH ₂ CH ₂) ₂ O	1.73	21,23)	85	85
43	C ₂ H ₅	C ₆ H ₅	H	N(CH ₂) ₄	0.62	21)	65	65
44	C ₂ H ₅	C ₆ H ₅	H	N(CH ₂ CH ₂) ₂ O	0.41	21,23)	60	65
45	i-C ₃ H ₇	C ₆ H ₅	H	N(CH ₂ CH ₂) ₂ O	-1.39	21)	20	6
46	c-C ₃ H ₇	C ₆ H ₅	H	N(CH ₂ CH ₂) ₂ O	-1.99	23)	12	8
47	C ₆ H ₅	Cl	C ₆ H ₅	N(CH ₂ CH ₂) ₂ O	-0.71	27)	33	a)
48	C ₆ H ₅	Br	C ₆ H ₅	N(CH ₂ CH ₂) ₂ O	0.0	27)	50	a)

a) Used for calibration. - b) From enthalpy differences. - c) At +99°C. - d) At -30°C; average of 14 *E/Z* pairs.

Table 3. Experimental and calculated *E/Z* equilibria of some Schiff bases 1
(X = C, Y = N, R³ = non-bonded electron pair)

Entry	R ¹	R ²	R ⁴	lnK	lit. ref.	% <i>E</i> exp.	% <i>E</i> calc.
49	H	CH ₃	CH ₃	>4.6	24,35)	>99	99.3
50	H	C ₆ H ₅	CH ₃	>4.6	28 - 31)	>99	>99.99
51	H	C ₆ H ₄ R-(4)	CH ₃	>4.6	30,32,33)	>99	>99.99
52	H	1-naphthyl	CH ₃	>4.6	30)	>99	98
53	H	C ₆ H ₃ (CH ₃) ₂ -(2,6)	CH ₃	2.75	30,32)	94	a)
54	H	C ₆ H ₂ (CH ₃) ₃ -(2,4,6)	CH ₃	2.44	30,32)	92	90
55	H	C ₆ H ₂ (CH ₃) ₃ -(2,4,6)	C ₆ H ₅	>3.9	24)	>98 ^{b)}	99.3 ^{c)}
56	H	C ₆ H(CH ₃) ₄ -(2,3,5,6)	CH ₃	1.59	30,32)	83	a)
57	H	C ₆ (CH ₃) ₅	CH ₃	1.32	30,32)	79 ^{d)}	82
58	H	C ₆ (CH ₃) ₅	C ₂ H ₅	1.73	32)	85	86
59	H	C ₆ (CH ₃) ₅	CH ₂ C(CH ₃) ₃	1.82	32)	86	87
60	H	C ₆ (CH ₃) ₅	CH(CH ₃) ₂	2.31	32)	91	88
61	H	C ₆ (CH ₃) ₅	t-C ₄ H ₉	>4.6	32)	>99	97
62a	H	9-anthryl	CH ₃	2.20	30,34)	90 ^{d)}	89
62b	H	9-anthryl	CH ₃	2.0	24)	88 ^{e)}	89
63	H	9-anthryl	C ₂ H ₅	2.44	30,34)	92	93
64	H	9-anthryl	CH ₂ C ₆ H ₅	2.44	24,34)	92	91
65	H	9-anthryl	CH ₂ C(CH ₃) ₃	2.59	30,34)	93	93
66	H	9-anthryl	CH(CH ₃) ₂	2.75	30,34)	94	93
67	H	9-anthryl	t-C ₄ H ₉	>4.6	30,34)	>99	99
68	H	9-anthryl	C ₆ H ₅	>3.9	24)	>98 ^{b,e)}	99 ^{e)}
69a	CH ₃	C ₂ H ₅	CH ₃	1.82	35)	86	87
69b	CH ₃	C ₂ H ₅	CH ₃	1.52	24)	82	87
70	CH ₃	C ₂ H ₅	CH ₂ C ₆ H ₅	1.59	24)	83	90
71	CH ₃	C ₂ H ₅	c-C ₆ H ₁₁	1.73	36)	85	92
72	CH ₃	C ₂ H ₅	C ₆ H ₅	1.39	41)	80	80
73	CH ₃	n-C ₃ H ₇	CH ₃	0.94	37)	72 - 85 ^{f)}	89
74	CH ₃	n-C ₃ H ₇	n-C ₄ H ₉	1.20	37)	77	93
75	CH ₃	n-C ₃ H ₇	c-C ₆ H ₁₁	1.66	36)	84	93
76	CH ₃	n-C ₃ H ₇	C ₆ H ₅	1.21	36)	77	82
77	CH ₃	CH ₂ CH(CH ₃) ₂	n-C ₄ H ₉	1.32	37)	79	92
78	CH ₃	CH ₂ CH(CH ₃) ₂	t-C ₄ H ₉	>4.6	36)	>99	99
79	CH ₃	CH ₂ C(CH ₃) ₃	n-C ₄ H ₉	2.09	37)	89	93
80	CH ₃	CH ₂ C(CH ₃) ₃	c-C ₆ H ₁₁	>4.6	36)	>99	93
81	CH ₃	CH ₂ C(CH ₃) ₃	C ₆ H ₅	>4.6	36)	>99	82
82	CH ₃	CH ₂ C ₆ H ₅	CH ₃	1.15	24,38)	76	78
83a	CH ₃	CH ₂ C ₆ H ₅	C ₆ H ₅	0.94	41)	70	72
83b	CH ₃	CH ₂ C ₆ H ₅	C ₆ H ₅	0.85	36)	72	72
84	CH ₃	CH ₂ C ₆ H ₅	1-naphthyl	1.10	24)	75 ^{c)}	75
85	CH ₃	CH(CH ₃) ₂	CH ₃	3.18	35)	96	95
86	CH ₃	CH(CH ₃) ₂	C ₆ H ₅	1.99	36)	88	90
87	CH ₃	c-C ₆ H ₁₁	c-C ₆ H ₁₁	2.59	36)	93	95
88	CH ₃	c-C ₆ H ₁₁	C ₆ H ₅	2.94	36)	95	84
89	CH ₃	CH(C ₆ H ₅) ₂	C ₆ H ₅	>4.6	36)	>99	87
90	CH ₃	t-C ₄ H ₉	CH ₃	>4.6	35)	>99	>99.99
91	CH ₃	t-C ₄ H ₉	c-C ₆ H ₁₁	>4.6	36)	>99	>99.99
92	CH ₃	t-C ₄ H ₉	C ₆ H ₅	>4.6	33,36)	>99	99.94
93a	CH ₃	C ₆ H ₅	CH ₃	2.59	28,29,39)	93	95
93b	CH ₃	C ₆ H ₅	CH ₃	2.89	31)	95	95
94	CH ₃	C ₆ H ₅	C ₆ H ₅	>2.2	93)	>90	≥90
95	CH ₃	C ₆ H ₄ R-(4)	CH ₃	2.94	29,39)	95 ^{g)}	95
96	CH ₃	C ₆ H ₄ NO ₂ -(4)	CH ₃	3.48	29,32,39)	97	95
97	CH ₃	C ₆ H ₄ NO ₂ -(4)	CH(CH ₃) ₂	2.94	29,32)	95	98
98	CH ₃	C ₆ H ₄ NO ₂ -(4)	t-C ₄ H ₉	3.89	29,32)	98	99.88
99	CH ₃	2-naphthyl	CH ₃	3.18	28,29)	96	a)

Table 3 (continued)

Entry	R ¹	R ²	R ⁴	lnK	lit. ref.	%E exp.	%E calc.
100a	CH ₃	1-naphthyl	CH ₃	-0.90	40)	29 ^{h)}	27
100b	CH ₃	1-naphthyl	CH ₃	-1.24	28,29)	22	27
101	CH ₃	1-naphthyl	CH ₂ C ₆ H ₅	-1.21	29)	23	24
102a	CH ₃	1-naphthyl	CH(CH ₃) ₂	-1.02	40)	26 ^{h)}	21
102b	CH ₃	1-naphthyl	CH(CH ₃) ₂	-1.15	29)	24	21
103	CH ₃	1-naphthyl	t-C ₄ H ₉	-0.58	29)	36	10
104	CH ₃	C ₆ H ₂ (CH ₃) ₃ -(2,4,6)	CH ₃	-2.94	29)	5	6
105	CH ₃	9-anthryl	CH ₃	-2.94	29)	5	5
106	C ₂ H ₅	CH ₂ C ₆ H ₅	C ₆ H ₅	-0.75	41)	32	38
107a	C ₂ H ₅	C ₆ H ₅	CH ₃	0.94	28,29)	74	75
107b	C ₂ H ₅	C ₆ H ₅	CH ₃	0.85	38)	70	75
108	C ₂ H ₅	C ₆ H ₅	CH ₂ C ₆ H ₅	0.45	40)	61 ^{h)}	78
109	C ₂ H ₅	C ₆ H ₅	C ₆ H ₅	2.75	24,42)	94 ⁱ⁾	69
110	C ₂ H ₅	C ₆ H ₄ NO ₂ -(4)	CH ₃	1.50	29)	81	75
111	C ₂ H ₅	C ₆ H ₄ R-(4)	CH ₃	1.15	29)	75	75
112a	C ₂ H ₅	1-naphthyl	CH ₃	-3.18	29,43)	4	5
112b	C ₂ H ₅	1-naphthyl	CH ₃	-	28)	0	5
113	C ₂ H ₅	CHCl ₂	c-C ₆ H ₁₁	2.31	44)	91	80
114	n-C ₃ H ₇	C ₆ H ₅	CH ₃	0.85	28,29)	70	72
115	n-C ₃ H ₇	CHCl ₂	c-C ₆ H ₁₁	2.44	44)	92	77
116	CH ₂ CH(CH ₃) ₂	CHCl ₂	c-C ₆ H ₁₁	1.52	44)	82	78
117	CH ₂ CH(CH ₃) ₂	CHCl ₂	C ₆ H ₅	-0.20	45)	45	68
118	CH ₂ C(CH ₃) ₃	CHCl ₂	c-C ₆ H ₁₁	-0.28	44)	43	77
119	CH ₂ C(CH ₃) ₃	CHCl ₂	C ₆ H ₅	>4.6	45)	>99	67
120	CH ₂ C ₆ H ₅	C ₆ H ₅	CH ₃	1.66	38)	84	85
121a	CH(CH ₃) ₂	C ₆ H ₅	CH ₃	-2.94	28,29)	5	1
121b	CH(CH ₃) ₂	C ₆ H ₅	CH ₃	<-4.6	46,47)	0	1
122	CH(CH ₃) ₂	C ₆ H ₅	C ₆ H ₅	-1.82	42)	14	3
123	CH(CH ₃) ₂	C ₆ H ₅	C ₆ H ₄ OCH ₃ -(4)	>4.6	46,47)	>99	3
124	CH(CH ₃) ₂	1-naphthyl	CH ₂ C ₆ H ₅	<-2.9	48)	<5	1
125	CH(CH ₃) ₂	CHCl ₂	c-C ₆ H ₁₁	-0.28	44)	43	53
126	CH(CH ₃) ₂	CHCl ₂	C ₆ H ₅	>4.6	45)	>99	52
127	s-C ₄ H ₉	C ₆ H ₅	H	-0.45	49)	39	15
128	s-C ₄ H ₉	CHCl ₂	c-C ₆ H ₁₁	-0.32	44)	42	58
129	s-C ₄ H ₉	CHCl ₂	C ₆ H ₅	>4.6	45)	>99	55
130	c-C ₆ H ₁₁	CHCl ₂	c-C ₆ H ₁₁	-0.49	44)	38	72
131	c-C ₆ H ₁₁	CHCl ₂	C ₆ H ₅	>4.6	45)	>99	64
132	t-C ₄ H ₉	C ₆ H ₅	CH ₃	<-4.6	28,29,43)	0	0
133	t-C ₄ H ₉	CHCl ₂	c-C ₆ H ₁₁	<-4.6	44)	0	0
134	C ₆ H ₅	C ₆ H ₄ R-(4)	CH ₃	- j)	29,50,51)	53-64	ca. 50
135	C ₆ H ₅	C ₆ H ₄ N(CH ₃) ₂ -(4)	CH ₃	0.90	29)	71 ^{d)}	ca. 50
136a	C ₆ H ₅	C ₆ H ₄ NO ₂ -(4)	CH ₃	0.67	40)	66 ^{h)}	ca. 50
136b	C ₆ H ₅	C ₆ H ₄ NO ₂ -(4)	CH ₃	0.62	29,50)	61-68	ca. 50
137	C ₆ H ₅	C ₆ H ₄ NO ₂ -(4)	t-C ₄ H ₉	0.80	40)	69 ^{k)}	ca. 50
138	C ₆ H ₅	C ₆ H ₄ OCH ₃ -(4)	C ₆ H ₄ R-(4)	0.5	33)	ca. 62 ^{l)}	ca. 50
139	C ₆ H ₅	1-naphthyl	CH ₃	<-4.6	29)	0	2 ^{m)}

a) Used for calibration. - b) At 60 and 200 MHz; temp. down to -40°C. - c) Calculated for coplanar phenyl. - d) Solvent-dependent. - e) Not temperature-dependent below room temp. - f) Temperature-dependent. - g) R = CH₃, C₆H₅, OCH₃, and Cl (average). - h) At ca. +190°C. - i) In CDCl₃ or nitrobenzene. - j) R = CH₃, CF₃, OCH₃, Cl, and Br. - k) At +89°C. - l) R = CH₃, N(CH₃)₂, and Cl. - m) Calculated with λ^d(C₆H₅) = 1.6.

Table 4. Experimental and calculated *E/Z* equilibria of some hydrazones and oxime derivatives 1
(X = C, Y = N, R³ = non-bonded electron pair)

Entry	R ¹	R ²	R ⁴	ln <i>K</i>	lit. ref.	% <i>E</i> exp.	% <i>E</i> calc.
140	CH ₃	C ₂ H ₅	NH ₂	1.27	52)	78	85
141	CH ₃	C ₂ H ₅	NHCH ₃	1.59	53)	83	85
142	CH ₃	C ₂ H ₅	NHC ₆ H ₅	1.73	54)	85 a)	85
143	CH ₃	C ₂ H ₅	NHR	1.66	55)	84 a,b)	85
144	CH ₃	C ₂ H ₅	NHC ₆ H ₃ (NO ₂) ₂ -(2,4)	1.39	55,56)	83,80	85
145	CH ₃	C ₂ H ₅	NHCONH ₂ or NHCSNH ₂	1.66	55)	84	85
146	CH ₃	C ₂ H ₅	N(CH ₃) ₂	1.52	57)	82 c)	84
147	CH ₃	C ₂ H ₅	N(CH ₃)C ₆ H ₅	1.82	58)	86 c)	88
148	CH ₃	C ₂ H ₅	OH	1.05	59)	74	79
149	CH ₃	C ₂ H ₅	OCH ₃	1.45	60)	81	79
150	CH ₃	n-C ₃ H ₇	NHC ₆ H ₃ (NO ₂) ₂ -(2,4)	1.39	55)	86	87
151	CH ₃	n-C ₃ H ₇	NHCONH ₂	1.52	55,56)	86,82	87
152	CH ₃	n-C ₃ H ₇	NH-aryl	1.82	55)	86 a)	87
153	CH ₃	n-C ₃ H ₇	OCH ₃	0.94	60)	72	80
154	CH ₃	CH ₂ CH(CH ₃) ₂	NHC ₆ H ₅	1.52	54)	82	87
155	CH ₃	CH ₂ CH(CH ₃) ₂	OCH ₃	1.05	60)	74	80
156	CH ₃	CH ₂ C(CH ₃) ₃	N(CH ₃)C ₆ H ₅	2.59	58)	93 c)	90
157	CH ₃	CH ₂ C(CH ₃) ₃	OCH ₃	1.15	60)	76	80
158	CH ₃	CH ₂ C ₆ H ₅	NH ₂	1.32	52)	79	76
159	CH ₃	CH ₂ C ₆ H ₅	NH-aryl	1.73	54,55)	85	76
160	CH ₃	CH ₂ C ₆ H ₅	NHC ₆ H ₃ (NO ₂) ₂ -(2,4)	1.32	55,56)	79,85	76
161	CH ₃	CH ₂ C ₆ H ₅	N(CH ₃)C ₆ H ₅	1.39	58)	80	79
162	CH ₃	CH ₂ C ₆ H ₅	OH	1.05	59)	74	70
163	CH ₃	CH ₂ C ₆ H ₅	OCH ₃	0.90	60)	71	70
164	CH ₃	CH(CH ₃) ₂	NH ₂	2.59	52)	93	94
165	CH ₃	CH(CH ₃) ₂	NHCH ₃	3.18	53)	96	94
166	CH ₃	CH(CH ₃) ₂	NH-aryl	2.94	54,55)	95 b)	94
167	CH ₃	CH(CH ₃) ₂	NHC ₆ H ₃ (NO ₂) ₂ -(2,4)	> 4.6	55)	> 99	94
168	CH ₃	CH(CH ₃) ₂	NHCONH ₂	2.20	56)	90	94
169	CH ₃	CH(CH ₃) ₂	N(CH ₃)C ₆ H ₅	2.75	58)	94 c)	95
170	CH ₃	CH(CH ₃) ₂	OH	2.31	59)	91	88
171	CH ₃	CH(CH ₃) ₂	OCH ₃	1.82	60)	86	88
172	CH ₃	CH(CH ₃) ₂	N(CH ₃) ₂	2.59	57)	93	93
173	CH ₃	t-C ₄ H ₉	NH ₂ or NHR	> 4.6	52-56)	> 99	99,99
174	CH ₃	t-C ₄ H ₉	OH or OCH ₃	> 4.6	59,60)	> 99	99,89
175	CH ₃	C ₆ H ₅	NHC ₆ H ₅	3.18	61)	96	94
176	CH ₃	C ₆ H ₅	NHC ₆ H ₃ (NO ₂) ₂ -(2,4)	0.53	56)	63	94
177	CH ₃	C ₆ H ₅	OH	2.75	59)	94	89
178	CH ₃	C ₆ H ₅	OCH ₃	3.89	60)	98	89
179	C ₂ H ₅	CH ₂ C ₆ H ₅	NHC ₆ H ₃ (NO ₂) ₂ -(2,4)	-0.20	55)	45	35
180	C ₂ H ₅	CH(CH ₃) ₂	NHC ₆ H ₃ (NO ₂) ₂ -(2,4)	1.39	55)	80	72
181	C ₂ H ₅	CH(CH ₃) ₂	OCH ₃	0.53	60)	63	66
182	C ₂ H ₅	c-C ₃ H ₅	NHC ₆ H ₃ (NO ₂) ₂ -(2,4)	0.62	56)	65	58
183	C ₂ H ₅	t-C ₄ H ₉	OCH ₃	> 4.6	60)	> 99	99,6
184	C ₂ H ₅	C ₆ H ₅	NHC ₆ H ₅	-0.04	61)	49	74
185	C ₂ H ₅	C ₆ H ₅	OH	2.44	59)	92	68
186	C ₂ H ₅	C ₆ H ₅	OCH ₃	1.66	60)	84	68
187	n-C ₃ H ₇	c-C ₃ H ₅	NHC ₆ H ₃ (NO ₂) ₂ -(2,4)	-0.20	56)	45	55
188	n-C ₃ H ₇	C ₆ H ₅	OCH ₃	1.39	60)	80	68
189	CH ₂ C ₆ H ₅	CH(CH ₃) ₂	NHC ₆ H ₃ (NO ₂) ₂ -(2,4)	1.52	55)	82	82
190	CH ₂ C ₆ H ₅	CH(CH ₃) ₂	OCH ₃	0.41	60)	60	75
191	CH(CH ₃) ₂	c-C ₃ H ₅	NHC ₆ H ₃ (NO ₂) ₂ -(2,4)	0.20	56)	55	35
192	CH(CH ₃) ₂	t-C ₄ H ₉	OH	> 4.6	59)	> 99	99,2
193	CH(CH ₃) ₂	C ₆ H ₅	NHC ₆ H ₅	-1.52	61)	18	1
194	CH(CH ₃) ₂	C ₆ H ₅	OCH ₃	-0.45	60)	39	3
195	t-C ₄ H ₉	C ₆ H ₅	NHC ₆ H ₅	< -4.6	61)	< 1	0

a) Solvent-dependent. - b) Average value of several R. - c) Not solvent-dependent.

Table 5. Experimental³²⁾ and calculated *E/Z* equilibria of some nitrones 1
($X = C, Y = N^{\oplus}, R^1 = H, R^2 = O^{\ominus}$)

Entry	R ²	R ³	lnK	% <i>E</i> exp.	% <i>E</i> calc.
196	C ₆ H ₃ (CH ₃) ₂ -(2,6)	CH ₃	-2.44	8	6
197	C ₆ H ₂ (CH ₃) ₃ -(2,4,6)	CH ₃	-2.31	9	9
198	C ₆ H(CH ₃) ₄ -(2,3,5,6)	CH ₃	-1.74	15	17
199	C ₆ (CH ₃) ₅	CH ₃	-1.59	17 ^{a)}	18
200	C ₆ (CH ₃) ₅	C ₂ H ₅	-2.09	11	11
201	C ₆ (CH ₃) ₅	CH ₂ C(CH ₃) ₃	< -4.6	<1	11
202	C ₆ (CH ₃) ₅	CH(CH ₃) ₂	-2.59	7	8
203	C ₆ (CH ₃) ₅	t-C ₄ H ₉	< -4.6	<1	1

a) Solvent-dependent.

preferable, but the frequently applied NMR integrations are rarely more precise than to $\pm 3\%$. Furthermore, it is not always certain whether equilibrium had been established. Whereas anils equilibrate rapidly, *N*-alkylimino compounds⁴⁰⁾ and enamines^{20,23)} may do so rather slowly.

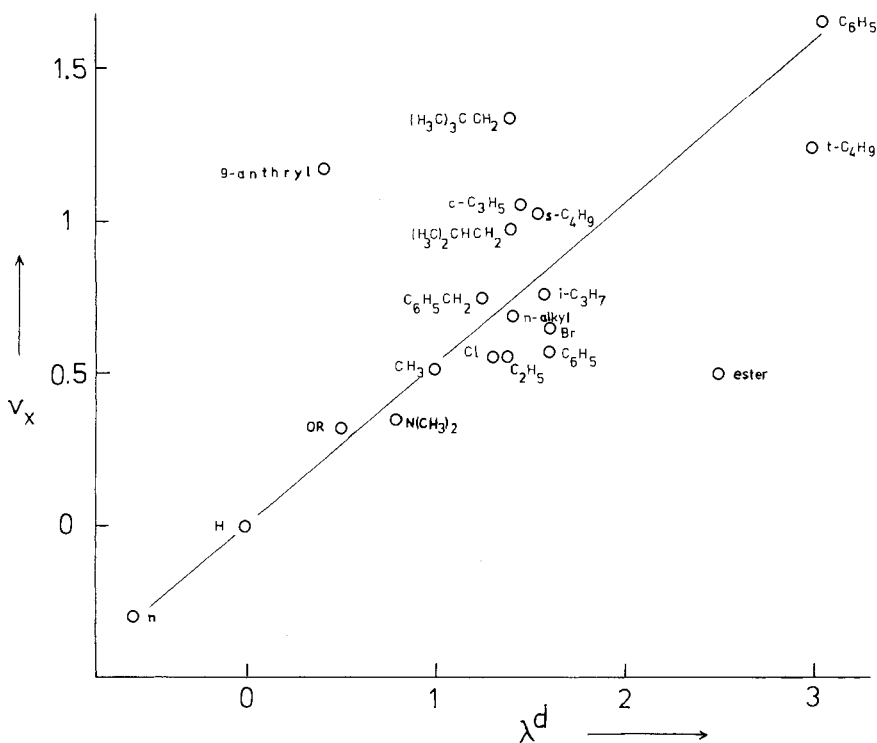


Figure 1. Relation of steric substituent parameters⁶²⁾ v_X to the corresponding λ^d values
(n = non-bonded electron pair as a substituent)

The double bond parameters λ^d in Table 1 are thus first estimates of differing quality and may be subject to a redetermination by more rigorous methods if additional, carefully measured data become available. Of the several sets of other substituent constants, the steric parameters v_x computed by Charton⁶²⁾ (but not Ugi's λ values) bear the closest resemblance to λ^d as shown in Figure 1, suggesting a predominantly steric interpretation for λ^d . Even the relative magnitude of the lone electron pair (n) turns out⁶³⁾ to be identical in both sets; the lone pair at sp^2 nitrogen had occasionally been found to be distinctly smaller than the sp^2 CH bond⁶⁴⁾. There is obviously no correlation of λ^d with inductive substituent constants σ_1 but more suitable examples will be reported subsequently⁴¹⁾.

A special problem is indicated by three different values in Table 1 for C_6H_5 (including *m*- and *p*-substitution). A coplanar, conjugated phenyl group is reasonably as „large“ as *tert*-butyl. If placed next to a *sec*- or *tert*-alkyl group, phenyl assumes a λ^d value between those of *o*-tolyl and $C_6(CH_3)_5$ or 9-anthryl. The least hindering, perpendicular conformation^{30,51)} favours the *Z*-isomer⁴³⁾ and is consistent with UV data; obviously it requires less space than methyl (Table 1). However, with neighbouring ethyl (entry 109) the correct choice of $\lambda^d(C_6H_5)$ may pose a problem.

Interestingly, NC_6H_5 groups in anils almost always take the perpendicular value ($\lambda^d = 0.6$). Loss of phenyl conjugation with the CN double bond can be mitigated by conjugative stabilization of the non-bonded electron pair at nitrogen, such that even the smallest substituents other than hydrogen can induce non-orthogonality. This perpendicular conformation is, however, not favoured in aldehyde anils⁶⁵⁾; therefore, λ^d of coplanar phenyl has to be used to explain the highly prepondering *E*-anils (entries 55 and 68) of those aldehydes for which measurable *E/Z* ratios were found in *N*-alkylimines (entries 54 and 62–66).

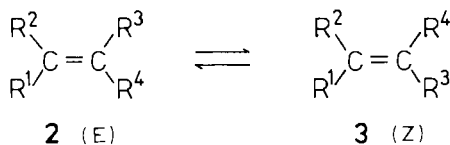
Naphthyl parameters for 1- or 2-junction are understandably very similar to phenyl values (Table 1); the nonplanar conformation of 1-naphthyl is beyond doubt⁴⁸⁾. A related dichotomy is also observed for amino substituents which are „large“ in enamines due to conjugation (see section D) but „small“ if situated at nitrogen in hydrazones. This difference may be less severe with strongly π -accepting β -substituents⁶⁶⁾ yet the special propensity of hydrazones^{66a)} towards non-planarity should be noted.

From the predictive tools contained in Table 1 it is possible to recognize special effects. It is now quite clear that the preponderance of the *Z*-isomer in certain β -enamino-carbonyl derivatives^{26,67,68)} is due to internal hydrogen bridging and therefore strongly solvent-dependent. In agreement with the calculated values, aldehyde hydrazones exist totally in the *E*-forms^{57,58)} if lacking an NH group. However, the *Z*-isomers are unexpectedly favoured or even predominant for all NH bearing acetaldehyde hydrazones^{52–55,61,69)} and oximes^{59,70)}. Preferential association of the *Z*-isomers^{54,70)} is certainly only one of the reasons for this since oxime ethers⁶⁰⁾ behave similarly. Prior to rationalizing these deviations from eq. (1) by the „*cis*-effect“ (section D), it will be shown that the model also has basic limitations.

C. Scope and Limitations

Notwithstanding the practical value of the heuristic eq. (1), it is instructive to connect our model with already tested ideas of substituent interactions in order to uncover some

of the conditions for its success or failure. Choosing olefins **2** and **3** for convenience of demonstration, we may assume that the concentrations (or activities and hence G°) of **2** and **3** may be described by eq. (9) and (10) since multiplicative combination of parameters has been shown to satisfy empirical free energy relationships like *Hammett's* or *Kessler's*⁷¹⁾. The mutual substituent interactions are expressed here as a sum of products of substituent constants a_i and of sensitivity factors characteristic of the geometrical substituent relations (g for geminal, c for *cis*, and t for *trans*). All other effects are thought to be the same (or constant) in *E*- and *Z*-forms.



$$-\ln[E] = \text{const} + g_E(a_1a_2 + a_3a_4) + c_E(a_1a_4 + a_2a_3) + t_E(a_1a_3 + a_2a_4) \quad (9)$$

$$-\ln[Z] = \text{const} + g_Z(a_1a_2 + a_3a_4) + c_Z(a_1a_3 + a_2a_4) + t_Z(a_1a_4 + a_2a_3) \quad (10)$$

$$\begin{aligned} \ln([E]/[Z]) &= (g_Z - g_E)(a_1a_2 + a_3a_4) + (c_Z - t_E)(a_1a_3 + a_2a_4) \\ &\quad + (t_Z - c_E)(a_1a_4 + a_2a_3) \end{aligned} \quad (11)$$

$$\ln([E]/[Z]) = (c - t)(a_1 - a_2)(a_3 - a_4) \quad (12)$$

Subtraction to give eq. (11) reveals that a simpler expression can only be derived for $g_E = g_Z$ and $c_Z - t_E = c_E - t_Z = c - t$, yielding eq. (12). Identifying a_i with $\lambda^d(i)$, we see that ρ of eq. (1) may be interpreted as the difference of *trans* and *cis* sensitivity factors. Although it may not be strictly correct to attach the same parameter a_i to a substituent like phenyl in both the *E*- and *Z*-isomer, the model can obviously absorb this ambiguity in practice.

The model will break down if one of the above conditions is not met; e. g., if t_E does not equal t_Z but $c_E = c_Z$. A striking example may be seen in 1,2-dichloroethene where eq. (1) fails because the negative experimental value⁷²⁾ can never be reproduced with any $\lambda^d(\text{Cl})$ if ρ is positive in eq. (13). The electronic destabilization⁷³⁾ peculiar to the *trans*-arrangement also accounts for the abnormal *E/Z*-ratios of some 1-halo-1-alkenes⁷²⁾, enol ethers⁷²⁻⁷⁴⁾, and perhaps alkyl nitrites⁷⁵⁾. A strong *trans*-destabilization⁷³⁾ might be expressed by a strongly positive t_E (or alternatively, t_Z) in eq. (9)–(11). Very special cases are then conceivable where the form of eq. (12) remains valid with $t > c$ to give a negative ρ value.

$$-0.53 = \ln([E]/[Z]) = \rho[\lambda^d(\text{Cl}) - \lambda^d(\text{H})]^2 \quad (13)$$

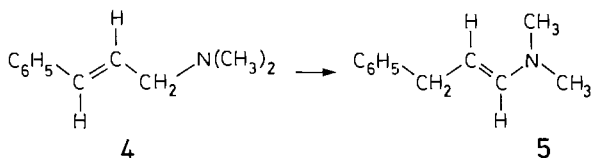
As a present limitation, Table 1 does not incorporate λ^d values applicable to strained systems like cyclic olefins. Failure of eq. (1) for imidates with the small $\lambda^d(\text{OR})$ of Table 1 remains presently unexplained since predominance either of the *Z*-⁷⁶⁾ or the *E*-forms⁷⁷⁾ have been reported.

D. Some Applications

General

The *E/Z* assignment of olefin stereoisomers is reliable if NMR coupling constants 3J can be observed. With Schiff bases or tri- and tetra-substituted olefins, chemical shift values can be misleading^{38,61} and long-range coupling constants may be sometimes ambiguous or unresolved. The predictive Table 1 and eq. (1) should hence be very helpful, provided that the stereoisomer in question is observed under equilibrium conditions, or nearly so. Thus, the *E* configuration may now be assigned with confidence to the minor isomer⁴⁹ (downfield NH shift) of the imine in entry 127. The claim that the anil of entry 123 should somewhat strangely be the pure *E*-isomer appears doubtful; indeed, almost all of the effects described⁴⁷) can be much more reasonably explained if the assignment of *E* and *Z* is reversed.

For substituents not contained in Table 1, the λ^d parameters may be estimated. E. g., λ^d (isopropyl) was used in entry 17 for 1-phenylethyl, and the oleic/elaidic esters of entry 14 as well as entries 30/31 may serve as further examples. On the other hand, the choice may be difficult for very similar substituents R^1 and R^2 (entries 134–138). In entries 34–36, λ^d (C_6H_5) = 1.6 must be used for R^2 because of bulky neighbours in both stereoisomers. For the enediamine of entry 39, the coplanar conformation of R^2 was chosen but perpendicular λ^d values for both R^3 and R^4 , as recommended⁷³). In all other enamines the amino group R^4 was regarded as coplanar even at the expense of a phenyl as R^3 ($\lambda^d = 0.6$). This implies that enamine conjugation in **5** is stronger than styrene conjugation in **4**, a result which is clearly confirmed by the practically complete isomerization²⁴) of **4** to **5**. A tentative $\lambda^d(CH_2COX) = 1.17$ may roughly account for hydrazone equilibria^{66b}).



The „*cis*-Effect“

Enol ethers^{72–74}) and oxime ethers⁶⁰) exhibit deviations from eq. (1) which in the absence of association by hydrogen bridges (section B) must be due to the „*cis*-effect“⁷³). The concept of electronic *trans*-destabilization⁷³) is applicable if both substituents at one end of the double bond have different donicity. Not surprisingly, therefore, oximes and oxime ethers of ketones are well-behaved (Table 4). On the other hand, there is no distinct evidence for the „*cis*-effect“ expected with $R^1 = \text{H}$ in enamines (Table 2), nitrones (Table 5), and enolates^{79–82}) (Table 6). The expected perturbation probably remained sufficiently small in these cases, such that it could have been absorbed in the λ^d parametrization, in contrast to the situation with 1-azaallyl anions⁴¹). The % values calculated with $\lambda^d(O^\ominus) = 0$ for entries 205–213 do not account for ion-pairing and solvent effects, of course. On the other hand, the 1-methylallyl anion (entry 204) is a 1 : 1 mixture of *E*- and *Z*-isomers in the gas phase⁷⁸).

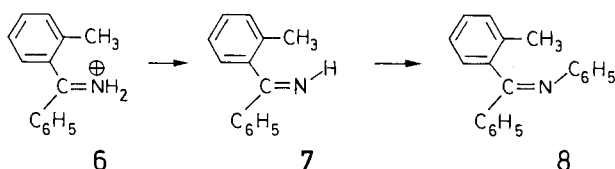
Table 6. Experimental and calculated *E/Z* equilibria of some enolates and of compounds **1** with *ortho*-substituted phenyl groups at the CN double bond (*n* = non-bonded electron pair)

Entry	XY	R ¹	R ²	R ³	R ⁴	ln <i>K</i>	lit. ref.	% <i>E</i> exp.	% <i>E</i> calc.
204	CC	H	CH ₃ [⊖]	H	CH ₃	0	78)	50	a)
205	CC	H	CH ₃	CH(CH ₃) ₂	OLi	< -4.6	79,80)	<1	18
206	CC	H	CH ₃	CH(CH ₃) ₂	OK	-1.67	79,80)	16	18
207	CC	H	C ₂ H ₅	CH(C ₂ H ₅) ₂	OK	-0.02	79)	49	11
208	CC	H	<i>n</i> -C ₄ H ₉	CH ₃	OLi	-1.08	79,80)	25	21
209	CC	H	<i>n</i> -C ₄ H ₉	CH ₃	OK	-1.34	79,80)	21	21
210	CC	H	CH(CH ₃) ₂	CH ₃	OK	-0.94	79)	28	18
211	CC	H	C ₆ H ₅	H	OK	-0.41	81)	40 ^{b)}	50
212a	CC	H	C ₆ H ₅	CH ₃	ONa	-2.20	82)	10 ^{c)}	5
212b	CC	H	C ₆ H ₅	CH ₃	ONa	≤ -2.44	82)	≤ 8 ^{d)}	5
213	CC	H	C ₆ H ₅	CH ₃	OK	< -2.9	81)	< 5 ^{b)}	5
214	CN	CH ₃	C ₆ H ₄ R-(4)	<i>n</i>	N(CH ₃) ₂	> 4.6	83)	> 99	93
215	CN	H	C ₆ H ₄ CH ₃ -(2)	<i>n</i>	CH ₃	> 4.6	30)	> 99	98
216	CN	CH ₃	C ₆ H ₄ CH ₃ -(2)	<i>n</i>	CH ₃	-1.15	28,29)	24	27
217	CN	CH ₃	C ₆ H ₄ CH ₃ -(2)	<i>n</i>	N(CH ₃) ₂	0.12	83)	53	30
218	CN	CH ₃	C ₆ H ₄ -C ₆ H ₅ -(2)	<i>n</i>	CH ₃	-0.32	39)	42	27
219	CN	CH ₃	C ₆ H ₄ CF ₃ -(2)	<i>n</i>	CH ₃	-0.90	39)	29	27
220	CN	CH ₃	C ₆ H ₄ NO ₂ -(2)	<i>n</i>	CH ₃	-0.28	29)	43	27
221	CN	CH ₃	C ₆ H ₄ OCH ₃ -(2)	<i>n</i>	CH ₃	-0.32	28,29)	42	27
222	CN	CH ₃	C ₆ H ₄ OCH ₃ -(2)	<i>n</i>	N(CH ₃) ₂	0.41	83)	60	30
223	CN	CH ₃	C ₆ H ₄ Cl-(2)	<i>n</i>	N(CH ₃) ₂	0.75	83)	68	30
224	CN	CH ₃	C ₆ H ₄ Br-(2)	<i>n</i>	N(CH ₃) ₂	0.28	93)	57	30
225	CN	C ₆ H ₅	C ₆ H ₄ CH ₃ -(2)	<i>n</i>	H	< -4.6	24,51)	< 1	≤ 18
226	CN	C ₆ H ₅	C ₆ H ₄ CH ₃ -(2)	<i>n</i>	CH ₃	< -4.6	29,51)	< 1	0
227	CN	C ₆ H ₅	C ₆ H ₄ CH ₃ -(2)	<i>n</i>	C ₆ H ₅	< -3.5	24)	< 3	≤ 5

a) Used for calibration. - b) In liq. ammonia at -20 °C. - c) In ether. - d) In tetrahydrofuran or *N,N*-dimethylformamide.

The „*ortho*-Effekt“

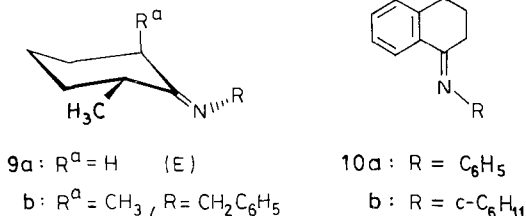
A group of phenomena related to a striking difference of *o*-substituted phenyl groups (entries 216–227) as compared to *p*- or unsubstituted ones (entry 214) have become known as the „*ortho*-effect“^{29,39,51,83}. This has been quantified in Table 6 with $\lambda^d = 0.8$ for C₆H₄R-(2) from Table 1, showing that the abnormal portion of the *E*-isomer is indeed explainable by reduced bulkiness^{39,51} in the perpendicular conformation. Evidence against an alternative interpretation^{29,30} by repulsive interaction of lone electron pairs with the aromatic π system must be postponed to a later paper. In this regard, Table 6 already shows that other donor or acceptor substituents at the *ortho*-position exert a less pronounced effect; this might be described by specific λ^d parameters but is not done here.



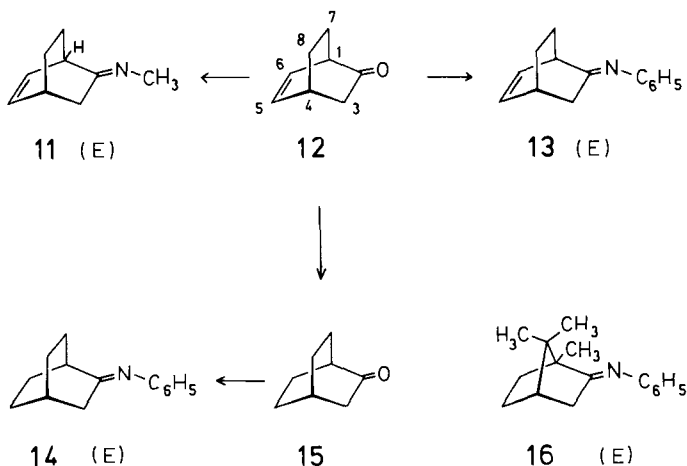
The reaction sequence **6** → **8** was used to prepare the imines of entries 225 and 227.

Schiff Bases of Some Cyclic and Bicyclic Ketones

The observation of 50–60% of *E*-isomer⁴⁷⁾ in iminocyclohexanes which are substituted at the 3,5-positions (but not at positions 2 and 6) is in accord with the calculated content of 50–51% of the *E*-form, taking from Table 1 the parameters for $n\text{-C}_3\text{H}_7$, $\text{CH}_2\text{CH}(\text{CH}_3)_2$, and $\text{CH}_2\text{C}(\text{CH}_3)_3$ substituents. With an equatorial 2-methyl in **9a**, a high *E* percentage is found^{47,84)} and also computed (99.96%) if $\lambda^d(t\text{-C}_4\text{H}_9)$ and $\lambda^d(n\text{-C}_3\text{H}_7)$ are used as an approximation to **9**; the *Z*-isomer can only be accommodated with an axial 2-methyl group⁸⁴⁾. Therefore, only the *trans*-2,6-dimethyl isomer is detected for **9b**⁸⁴⁾. The downfield NMR shifts observed at the lone-pair side as expected⁸⁵⁾ support the assignments; the reported, somewhat confusing spin-spin splitting patterns^{47,84)} could result from virtual coupling⁸⁶⁾ and hence be of no immediate significance.



The proposal⁸⁵⁾ that 1-(phenylimino)indan as well as **10a** and **b** are pure *E*-isomers can now be confirmed by calculation (>99.7% *E*).



The two diastereotopic protons in the $\text{CH}_2\text{-3}$ group of **12**⁸⁷⁾ probably possess accidentally equal rather than different⁸⁸⁾ chemical shifts since their line separation is found at 60 MHz to be the same as at 100 MHz; only a very small shift difference has

been reported for bicyclo[2.2.2]octene⁸⁹. Corresponding CH₂-3 isochronism is found in imines **11** and **13**, and confirmed by double-resonance experiments. The CH₂-3 assignments in **11** – **14** were further proven by base-catalyzed H/D exchange under conditions not sufficiently severe to cause rearrangement *via* homoenolization⁹⁰; these experiments also served to show the coincidence in **14** of the non-exchangeable 1-H signal (*E*-isomer) with the CH₂-3 doublet of the *Z*-isomer.

Deshielding of both the 1-H and CH₂-3 protons adjacent to the anisotropic⁸⁵ carbonyl and imino functions in **11** – **14** and **15**⁹¹) amounts to ca. 0.5 ppm. Nevertheless it is surprising that **11** shows no shift differences indicative of two isomers; likewise, the *syn*- and *anti*-CH₂ groups in *N*-methylcyclohexylideneamine⁸⁵) were accidentally isochronous. The coupling constant ⁵*J* = 1.15 Hz between the NCH₃ and CH₂-3 groups of **11** must be interpreted with care because of its very high angular dependence⁹²; the content of 71% of the *E*-isomer calculated with CH₂CH(CH₃)₂ and CH(CH₃)₂ values is thus neither invalidated nor directly supported experimentally.

The same calculation predicts 66% of the *E*-isomer for the anils **13** and **14**. The experimental values are 69 and 76%, respectively. Although the minor *Z*-forms are characterized by downfield CH₂-3 shifts, this criterion⁹³) fails for the almost equally shifted bridgehead protons of *E*- and *Z*-**13** (identification by decoupling). Camphoranil (**16**), exhibiting only 3 equally intense methyl signals⁹⁴), consists of at least 85% of the *E*-isomer as expected (99.74%) for *tert*-butyl and isopropyl as the flanking substituents.

I thank the *Stiftung Volkswagenwerk* for providing an NMR spectrometer HA-60-IL.

Experimental Part

N,N-Dimethyl-3-phenyl-1-propen-1-amine (**5**, Entry 32): The general method of *Sauer and Prahl*²⁰) was used since neither the aminonitrile route⁹⁵) nor TiCl₄ catalysis⁹⁶) proved successful. An exothermic reaction ensued on slow addition of cinnamyl bromide⁹⁷) in ethanol to excess aqueous dimethylamine. Dilution with aqueous sodium hydroxide, ether extraction, washing, and drying over potassium carbonate yielded 63% of **4** with b.p. 111–114°C/14 Torr (lit.⁹⁸) 100–101°C/7 Torr). – ¹H-NMR (CCl₄): δ = 7.24 (m, C₆H₅), 6.40 (d, ³*J* = 16 Hz), 6.16 (dt, ³*J* = 16 and 5.5 Hz), 2.98 (d, ³*J* = 5.5 Hz, CH₂), 2.17 (s, dimethylamino).

2.00 g (12.4 mmol) of **4** and 3.68 mmol²⁰) of potassium *tert*-butoxide were stirred in 6.0 ml of anhydrous dimethyl sulfoxide under nitrogen for 15 hours. Work-up with ether and aqueous sodium hydroxide, drying over potassium hydroxide, and distillation at 115–120°C bath temperature/12 Torr (lit.⁹⁹) 58–60°C/0.6 Torr) yielded 43% **5** as a pale yellow, unstable liquid. – ¹H-NMR (DCCl₃): δ = 7.08 (s, C₆H₅), 5.83 (dt, ³*J* = 13.5 and ⁴*J* = 1.0 Hz), 4.20 (dt, ³*J* = 13.5 and 7 Hz), 3.21 (d, ³*J* = 7 Hz, CH₂), 2.50 (s, dimethylamino).

N-Ethylidenemethanamine (Entry 49): An almost pure sample was obtained as described¹⁰⁰) with b.p. 27–30°C (lit.¹⁰¹) 27–31°C). Measurement of the NMR spectrum under literature¹⁰⁰) conditions revealed ⁴*J* = 1.52 Hz as the only deviation, and no change at –78°C.

N-(2,4,6-Trimethylphenylmethylene)benzenamine (Entry 55): Prepared from 2,4,6-trimethylbenzaldehyde¹⁰²) and recrystallized from methanol with m.p. 48–49°C (lit.¹⁰³) 49°C, lit.¹⁰⁴) 50–52°C), yield 50%. – ¹H-NMR (DCCl₃ at +26, –8, and –51°C): δ = 8.71 (s, aldimine), 7.21 (m, C₆H₅), 6.87 (s, *m*-H), 2.50 (s, 2-CH₃), 2.27 (s, 4-CH₃).

N-(9-Anthrylmethylene)methanamine (Entry 62b): A sample with m.p. 104–107°C was obtained which showed no impurities (lit.³⁰) 113°C). – ¹H-NMR (DCCl₃ at –37°C): δ = 9.25 (q, ⁴*J*

= 1.7 Hz, 89% aldimine *E*), 9.12 (m, 11% aldimine *Z*), 8.40 (m and s, 1', 8', and 10'-H), 7.94 (m, 4'- and 5'-H), 7.45 (m, 2', 3', 6', and 7'-H), 3.76 (d, $^4J = 1.71$ Hz, 89% $\text{NCH}_3(\text{E})$), 3.05 (d, $^4J = 2.19$ Hz, 11% $\text{NCH}_3(\text{Z})$).

N-(9-Anthrylmethylene)-1-phenylmethanamine (Entry 64): Light yellow needles prepared¹⁰⁵) in 62% yield with m. p. 86–87.5 °C from ethanol (lit.³⁰) 72–73 °C; lit.¹⁰⁵) 88 °C). – $^1\text{H-NMR}$ (DCCl_3): $\delta = 9.41$ (t, $^4J = 1.40$ Hz, aldimine), 8.42 (m and s, 1', 8', and 10'-H), 7.89 (m, 4'- and 5'-H), 7.35 (m, C_6H_5 , 2', 3', 6', and 7'-H), 5.02 (d, $^4J = 1.40$ Hz, 92% $\text{CH}_2(\text{E})$), 4.31 (m, 8% $\text{CH}_2(\text{Z})$).

N-(9-Anthrylmethylene)benzenamine (Entry 68): Bright yellow needles with m. p. 112.5–113 °C from ethanol (lit.¹⁰⁵) 112 °C; lit.¹⁰⁶) 113.5–115 °C). – $^1\text{H-NMR}$ (DCCl_3 at –51 °C): $\delta = 9.59$ (s, aldimine), 8.70 (m, 1'- and 8'-H), 8.52 (s, 10'-H), 8.05 (m, 4' and 5'-H), 7.53 (m and s, 2', 3', 6', 7'-H, and C_6H_5).

N-(1-Methylpropylidene)methanamine (Entry 69b): A mixture of 2-butanone and excess aqueous methylamine¹⁰⁷) was saturated with solid potassium hydroxide in the course of 2 days. Distillation at 84–88 °C (lit.¹⁰⁸) 87 °C) yielded 60% of colourless liquid. The published¹⁰⁸) NMR spectrum had to be re-assigned according to lit.³⁵): $^1\text{H-NMR}$ (DCCl_3): $\delta = 3.08$ (m, NCH_3), 2.27 (qq, $^3J = 7.6$ and $^5J = 1.25$ Hz, CH_2 of *E*, *Z* not resolved), 1.97 (broad q, $^5J = 1.35$ Hz, 18% $\text{CCH}_3(\text{Z})$), 1.80 (q, $^5J = 0.79$ Hz, 82% $\text{CCH}_3(\text{E})$), 1.07 (t, $^3J = 7.6$ Hz, $\text{CH}_3(\text{E})$), 1.05 (t, $^3J = 7.6$ Hz, $\text{CH}_3(\text{Z})$).

N-(1-Methylpropylidene)-1-phenylmethanamine (Entry 70): A benzene solution of 2-butanone and 2 equivalents of benzylamine was saturated with solid potassium hydroxide, dried, and distilled to yield 45% of slightly yellow liquid, b. p. 72 °C/0.3 Torr (lit.¹⁰⁹) 74–80 °C/0.7 Torr). The NMR spectrum¹⁰⁹) had to be re-assigned: $^1\text{H-NMR}$ (DCCl_3): $\delta = 7.20$ (m, C_6H_5), 4.42 (broad s, NCH_2), 2.30 (qm, $^3J = 7.4$ Hz, CCH_2 , *E* and *Z* not resolved), 2.02 (t, $^5J = 1.33$ Hz, 17% $\text{CCH}_3(\text{Z})$), 1.80 (t, $^5J = 0.76$ Hz, 83% $\text{CCH}_3(\text{E})$), 1.08 (t, $^3J = 7.4$ Hz, $\text{CH}_3(\text{E})$), 1.03 (t, $^3J = 7.6$ Hz, $\text{CH}_3(\text{Z})$).

N-(1-Methyl-2-phenylethylidene)methanamine (Entry 82): The pale yellow liquid distilling at 97–98 °C/12 Torr (lit.³⁸) 42–43 °C/0.1 Torr) showed an NMR spectrum in DCCl_3 at –51 °C practically identical with the published³⁸) one in pyridine.

N-(1-Methyl-2-phenylethylidene)-1-naphthalenamine (Entry 84): The solution of 20 mmol of 1-aminonaphthalene, 20 mmol of phenylacetone, and 27 mmol of pulverized sodium cyanide in 25 ml of glacial acetic acid was stirred overnight. After dilution with iced water and repeated extraction with methylene chloride, the organic layer was washed with a solution of NaHCO_3 and dried over sodium sulfate. Colourless, rod-shaped crystals of 2-Methyl-2-(1-naphthylamino)-3-phenylpropionitril were obtained in 49% yield with m. p. 102.5–104 °C (cyclohexane, then methanol). – IR (KBr): 3380 (NH, sharp), 3059, 3030, 2980, 2937 (CH); 2220 (CN); 1582, 1520, 1480, 1417, 1253, 770, 707 cm^{-1} . – $^1\text{H-NMR}$ (CCl_4): $\delta = 7.60$ and 7.24 (m, intensities 2 and 10), 4.09 (broad s, NH), 3.33 and 3.13 (AB spectrum, $^2J = 13.5$ Hz, CH_2), 1.65 (s, CH_3).

$\text{C}_{20}\text{H}_{18}\text{N}_2$ (286.4) Calcd. C 83.88 H 6.33 N 9.78 Found C 84.26 H 6.52 N 9.81

This aminonitrile was subjected to elimination of hydrogen cyanide as described subsequently⁴¹). Treatment with sodium ethoxide in anhydrous ethanol for 1 hour at 60 °C, subsequent dilution with iced water, and extraction by methylene chloride yielded the oily title imine with b. p. 150–180 °C bath temperature/0.005 Torr; purity ca. 85%. – $^1\text{H-NMR}$ (CCl_4): $\delta = 7.30$ (mc), 3.78 (s, 75% $\text{CH}_2(\text{E})$), 3.33 (s, 25% $\text{CH}_2(\text{Z})$), 2.13 (s, $\text{CH}_3(\text{Z})$), 1.60 (s, $\text{CH}_3(\text{E})$); no change at –40 °C.

N-(1-Phenylpropylidene)benzenamine (Entry 109): A sample prepared as described³⁸) had m. p. 47–52°C (lit.³⁸) 45–47°C). – ¹H-NMR (DCCl₃): δ = 7.90 (m, *o*-H of C₆H₅), 7.4–6.7 (m, intensity 8), 2.56 (q, ³*J* = 7.5 Hz, CH₂), 1.15 (t, 6% CH₃(*Z*)), 0.98 (t, ³*J* = 7.5 Hz, 94% CH₃(*E*)).

[[2-Methylphenyl]phenylmethylene]ammonium chloride (**6**): 10.0 g (86 mmol) of 2-methylbenzotrile in 50 ml of anhydrous ether was added dropwise to 103 mmol of phenylmagnesium bromide in 75 ml of anhydrous ether. The mixture was refluxed for 1 hour and chilled. On acidification with hydrochloric acid, a precipitate was collected and washed with a small quantity of ethanol; crude yield 99%. Separation from ammonium chloride was achieved by recrystallization from anhydrous ethanol to give **6** with m. p. 222–226°C (lit.¹¹⁰) 222–224°C). – ¹H-NMR (DCCl₃): δ = 11.6 (broad s, NH₂[⊕]), 8.03 (dm, 2 *o*-H), 7.45 (m), 2.23 (s, CH₃).

1-(2-Methylphenyl)-1-phenylmethanimine (**7**, Entry 225): A small sample of **6** was shaken with excess aqueous sodium hydroxide, crushed ice, and methylene chloride. The dried organic layer was evaporated to yield **7** as an oil containing a trace of 2-methylbenzophenone. – ¹H-NMR (CCl₄): δ = 9.20 (broad s, NH), 7.61 (m, 2 *o*-H), 7.16 (m), 2.07 (s, CH₃); no change at –27°C.

N-[[2-Methylphenyl]phenylmethylene]benzenamine (**8**, Entry 227): The solution of 25 mmol of **6** and 25.5 mmol of aniline in 30 ml of anhydrous benzene was refluxed for 20 hours. After evaporation of the filtered benzene solution, the solid residue was crystallized from cyclohexane to give **8** as colourless cubes with m. p. 103–105°C in 41% yield. – IR (KBr): 3060, 3025, 2918, 1623 (CN), 1590, 1575, 1483, 1445, 760, 690 cm⁻¹. – UV (cyclohexane): λ_{max} (lg ε) = 251 (4.26) and 334 nm (3.49). – ¹H-NMR (CCl₄): δ = 7.66 (m, 2 *o*-H), 7.30–6.56 (m, intensity 12), 1.97 (s, CH₃).

C₂₀H₁₇N (271.3) Calcd. C 88.52 H 6.32 N 5.16 Found C 88.84 H 6.18 N 5.03

Bicyclo[2.2.2]oct-5-en-2-one (**12**): The improved procedure⁸⁷) yielded **12** with m. p. 72–79°C (lit.⁸⁷) 84–86°C) which was spectroscopically pure. – ¹H-NMR (DCCl₃, dioxane, or CCl₄, 100 or 60 MHz): δ = 6.43 and 6.15 (m, olefinic 5- and 6-H), 2.99 (m, 1- and 4-H), 1.93 (dd, ³*J* = 2.7 and ⁴*J* = 1 Hz, CH₂-3), 1.63 (m, CH₂-7 and -8). – The CH₂-3 signal disappeared completely on heating to 100°C with NaOD/D₂O in dioxane for 1 hour.

N-(Bicyclo[2.2.2]oct-5-en-2-ylidene)methanamine (**11**): 30 mmol of **12**, 10 mmol of methylammonium chloride¹⁰⁷), and 200 mmol of aqueous methylamine were stirred in an ice bath for 2 hours. After addition of 100 ml of diethyl ether and of solid potassium hydroxide, the ether layer was dried over KOH and distilled to give 70% of **11** with b. p. 83–87°C/19 Torr as a clear, colourless liquid. – IR (film): 3045, 2940, 2902, 2865, 1668 (CN), 1610, and 697 cm⁻¹. – ¹H-NMR (CCl₄): δ = 6.23 (A-part of AA'XX', 5- and 6-H), 3.08 and 2.83 (2 m, 1- and 4-H), 2.83 (t, ⁵*J* = 1.15 Hz, CH₃), 1.93 (broad s, CH₂-3), 1.52 (mc, CH₂-7 and -8). A clean singlet for NCH₃ was obtained on irradiation of CH₂-3.

C₉H₁₃N (135.2) Calcd. C 79.95 H 9.69 N 10.36 Found C 79.56 H 9.58 N 10.39

N-(Bicyclo[2.2.2]oct-5-en-2-ylidene)benzenamine (**13**): A water trap condenser was charged with 120 mmol of **12**, 224 mmol of aniline, 11 mmol of anilinium chloride, and 70 ml of xylene. After 4 hours of refluxing, washing of the ethereal solution with aqueous sodium hydroxide and water, drying, and fractional distillation, a pale yellow oil was obtained, yield 65%; b. p. 165–195°C/12 Torr or 120–130°C/0.001 Torr. – IR (film): 3055, 2941, 2902, 2865, 1664 (CN), 1592, 1486, and 696 cm⁻¹. – ¹H-NMR (60 or 100 MHz, CCl₄ or DCCl₃): δ = 7.09 (m, 3 aromat. H), 6.59 (dm, 2 aromat. H), 6.31 (m, 5'- and 6'-H), 3.33 and 3.25 (2 m, 1'-H *E* and *Z*), 2.82 and 2.72 (2 m, 4'-H *Z* and *E*), 2.23 (d, ³*J* = 2.7 Hz, 31% CH₂-3' of *Z*), 1.85 (d, ³*J* = 2.7 Hz, 69% CH₂-3' of *E*), 1.52 (mc, CH₂-7' and -8'). – Only the first two groups of signals were smaller

in a sample prepared from aniline partially deuterated in *o,p*-position. – H/D exchange at both CH₂-3' groups with NaOCH₃ in CH₃OD occurred quickly at 25°C with complete signal disappearance at 100°C.

Decoupling experiments: Both CH₂-3' doublets became sharp singlets on irradiating 4'-H, the 4'-H signal a quintet on irradiating 5'- and 6'-H, and only the 5'-/6'-H signal simplified on irradiating 1'-H.

C₁₄H₁₅N (197.3) Calcd. C 85.24 H 7.66 N 7.10 Found C 84.81 H 7.63 N 7.37

Bicyclo[2.2.2]octan-2-one (15): A sample prepared in 97% yield by catalytic hydrogenation of 12 in methanol over Raney nickel was spectroscopically pure; m.p. 150–167°C (lit.¹¹¹) 178–179°C). – ¹H-NMR (CCl₄): δ = 2.13 (s, 1-H and CH₂-3)⁹¹, 1.72 and 1.50 (structureless m, 4-H to 8-H). – ¹H-NMR (FSO₃H)¹¹²): δ = 3.27 (broad, 1-H), 3.17 (d, ³J = 3 Hz, CH₂-3), 2.7–1.8 (m, intensity 9).

N-(Bicyclo[2.2.2]octan-2-ylidene)benzenamine (14): B.p. 165°C/12 Torr (lit.¹¹³) 168 to 171°C/20 Torr). – ¹H-NMR (CCl₄): δ = 7.05 (m, 3 aromat. H), 6.60 (m, 2 aromat. H), 2.43 (d + m, ³J = 2.8 Hz, CH₂-3' of Z and 1'-H of E), 2.05 (d, ³J = 2.5 Hz, CH₂-3' of E), 1.64 (m, 4'-H to 8'-H). – Both CH₂-3' doublets disappeared with NaOCH₃ in CH₃OD at 100°C whereas m at δ = 2.43 remained.

N-(2-Bornanylidene)benzenamine (16): B.p. 160–164°C/12 Torr (lit.¹¹⁴) 164.5 to 166°C/15 Torr); yield 32%. The NMR spectral data⁹⁴) were confirmed.

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