Kurze Mitteilungen

Bis am 15. des Monats bei der Redaktion eingehende Kurze Mitteilungen werden in der Regel am 15. des folgenden Monats veröffentlicht. Es werden auch Manuskripte aus dem Ausland angenommen. Maximalumfang: 6 Schreibmaschinenseiten (alles inbegriffen)

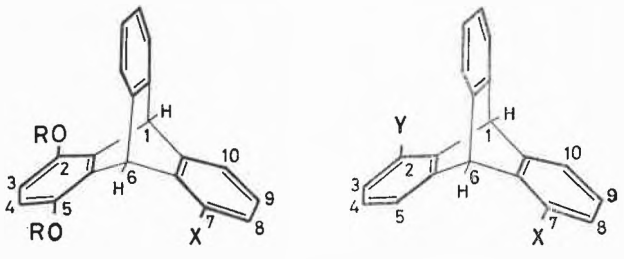
The Absolute Configuration of 2,7-Disubstituted Triptycenes as Determined by the Chemical Correlation*

Summary

The absolute configuration of optically active 2,5,7-trisubstituted triptycenes deduced from the rigorous analysis of their CD spectra based on molecular exciton theory was found to be consistent with that determined by "the revised X-ray method". In order to get further information, the absolute configuration of 2,7-discustituted triptycene was correlated with that of 2,5,7-trisubstituted triptycenes.

The present authors have reported the synthesis, optical resolution of 2,5-diacetoxy-7-carboxytriptycene (I)[1] and the preparation of a series of optically active 7-substituted-2,5-dimethoxytriptycenes starting from (+)-I[2]. They are reasonably regarded as one of the ideally suited compounds for the study of optical rotatory properties. (+)-2,5-Dimethoxy-7-dimethylaminotriptycene hydrobromide (III) thus prepared has been studied by the X-ray structure analysis[3], indicating 1S, 6R absolute configuration by "the revised X-ray method" (Fig. 1)[4]. The rigorous analysis of CD spectra of this series of compounds afforded consistent configuration with that determined by "the revised X-ray method"[5]. The preceding paper presents a similar CD analysis of the absolute configuration performed on 2,7-disubstituted triptycenes.

The present paper deals with the transformation of 2,7-disubstituted triptycene to 2,5,7-trisubstituted derivative performed with the purpose to establish the correlation of absolute configuration between the series of di- and trisubstituted triptycenes.



(+)-I, R = CH_3CO, X = COOH
(+)-II, R = CH_3, X = $COOCH_3$
(+)-III, R = CH_3, X = $N(CH_3)_2HBr$

(+)-VI_b, X = Y = COOH
(+)-VI_d, X = OCH_3, Y = COOH
(+)-VI_e, X = Y = NH_2
(+)-VI_f, X = Y = CH_3

Fig. 1

Starting from 1,5-dichloroanthraquinone (IV_a), 1,5-dimethoxycarbonylanthracene (V_b) was obtained in 4 steps via IV_b, IV_c and V_a. The reaction of V_b with benzyne yielded 2,7-dimethoxycarbonyltriptycene [VI_a, mp 209–209.5°] which gave 2,7-dicarboxytriptycene [VI_b, mp 332–335°] on hydrolysis. VI_b was resolved with cinchonidine and cinchonine to give (+)-VI_b [mp 342.5–350° (dec.), $[\alpha]_D^{15}$ + 33.3° (c, 0.543, CH_3OH)] and (−)-VI_b [mp 342–350° (dec.), $[\alpha]_D^{15}$ − 33.9° (c, 0.543, CH_3OH)], respectively[6]. Similarly (±)-VI_d [mp 255° (dec.)] was obtained from anthraquinone-1-carboxylic acid (IV_d) in 6 steps ($IV_d \rightarrow IV_e \rightarrow IV_f \rightarrow V_c \rightarrow V_d \rightarrow VI_c \rightarrow VI_d$). Optical resolution of (±)-VI_d with brucine afforded (+)-VI_d [mp 267°, $[\alpha]_D^{20}$ + 15.4°, $[\alpha]_{405}^{20}$ − 74.4° (c, 0.187, dioxane)][7].

The absolute configuration of VI_b and VI_d was determined by chemical correlation with (+)-II, i.e., with (+)-7-substituted-2,5-dimethoxytriptycenes.

* Eingegangen am 25. Juli 1972.

[1] A. Sonoda, F. Ogura, and M. Nakagawa, *Bull. Chem. Soc. Japan* *35* (1962) 853.
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[5] J. Tanaka, K. Ozeki-Minakata, F. Ogura, and M. Nakagawa, to be published.
[6] Y. Sakata, F. Ogura, and M. Nakagawa, to be published.

(+)-Dicarboxylic acid (VI_b) was treated with equimolar sodium methoxide and the resulting acidic salt was converted into half-ester [(+)-$VIII_a$, mp 252°] by the reaction with dimethyl sulfate. The Curtius reaction of (+)-VII_b derived from (+)-VII_a gave (+)-aminocarboxylic acid (VII_e) *via* VII_c and VII_d. Esterification of (+)-VII_e afforded (+)-aminomethyl ester [VII_f, mp 161–162°]. Diazotization of (+)-VII_f followed by hydrolysis of diazonium salt gave (+)-hydroxy acid [VII_g, mp 269–271°] which was converted into methyl ester [VII_h, mp 217–225°]. Methylation of (+)-VII_g yielded (+)-methoxy methyl ester [VII_i, mp 240–241°. Found: C, 80.44; H, 5.42%. Calcd. for $C_{23}H_{18}O_3$: C, 80.68; H, 5.30%. CD: λ_{max}^{MeOH} ($\Delta\varepsilon$) 314–290 (broad peak, +0.4), 276 (+2.51), 262 (−2.05), 232 (+12.6) nm].

(+)-VII_h was coupled with diazotized sulfanilic acid and the resulting (+)-azo compound (VIII) was reduced to yield (+)-aminophenol (IX). Oxidation of (+)-IX with ferric sulfate afforded (+)-quinone ester (X) which could be reduced to (+)-hydroquinone derivative (XI_a). Methylation of (+)-XI_a gave (+)-2,5-dimethoxy-7-methoxycarbonyltriptycene [XI_b, mp 261.5–262.5°. Found: C, 77.55; H, 5.46%. Calcd. for $C_{24}H_{20}O_4$: C, 77.40; H, 5.41%. CD: $\lambda_{max}^{dioxane}$ ($\Delta\varepsilon$) 303 (+1.61), 280 (+0.57), 267 (−3.06), 262 (−2.66) nm].

A series of optically active triptycenes, retaining C_2 axis of symmetry, such as VI_e and VI_f were prepared starting from (+)-VI_b[7].

The fact that (+)-XI_b and (+)-VI_c are identical in every respect with (+)-II and (+)-VII_i, respectively, established the correlation of absolute configuration between above-mentioned 2,7-disubstituted and 2,5,7-trisubstituted triptycenes. In view of the 1S,6R absolute configuration of (+)-III, the absolute configuration of (+)-VI_b and (+)-VI_d is concluded to be 1S,6S shown in Fig. 2, being consistent with the results of CD analysis

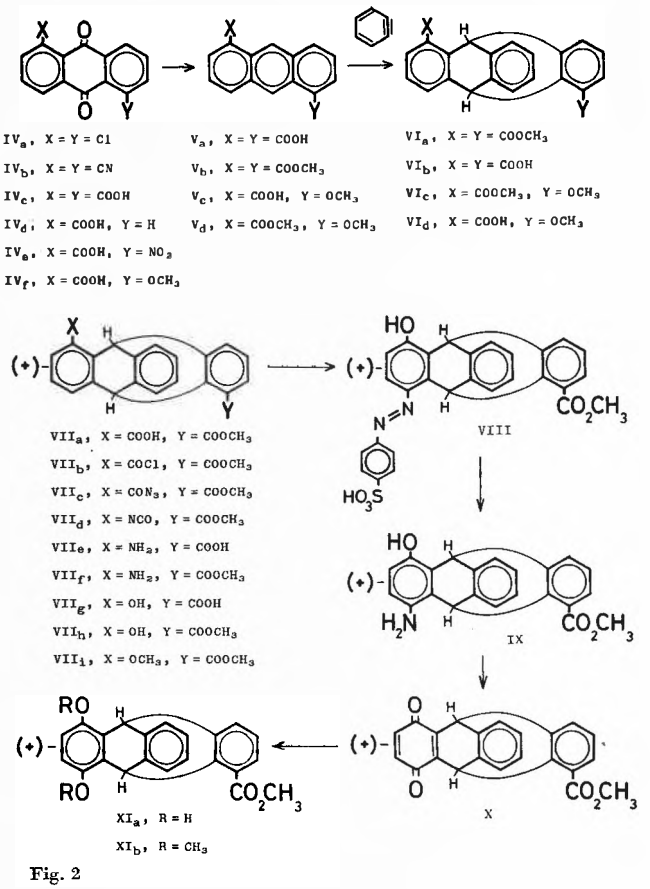

Fig. 2

of this series of 2,7-disubstituted triptycenes as is shown in the preceding paper.

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[7] M. KURITANI, Y. SAKATA, F. OGURA, and M. NAKAGAWA, to be published.

The Circular Dichroism and the Absolute Configuration of 2,7-Disubstituted Triptycenes*

Summary

The absolute configurations of (+)2,7-disubstituted triptycenes are determined by the CD spectral analysis. The result is not in agreement with the absolute configuration determined by the chemical correlation method combined with the X-ray result. This finding provides an additional support to our proposal that the current method of determining the absolute configuration by the X-ray method should be changed so as to give the antipodal configuration.

Triptycene derivatives are optically active when substituted dissymmetrically into the benzene rings (Fig. 1). The coupling of the benzene chromophores gives molecular exciton states, and the chirality of the component transition moments on each benzene rings is an origin of the optical activity. Recently we have carried out a systematic investigation of triptycene derivatives with

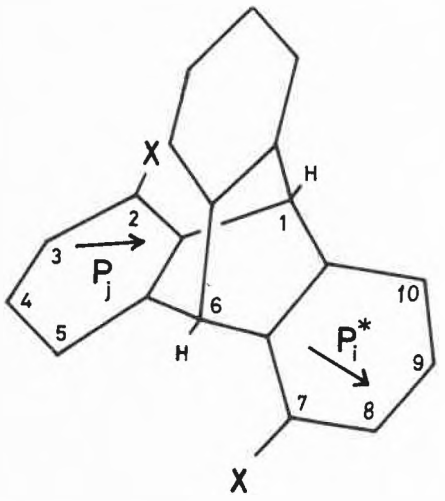

Fig. 1. Absolute Configuration of (+)-2,7-Disubstituted Triptycenes

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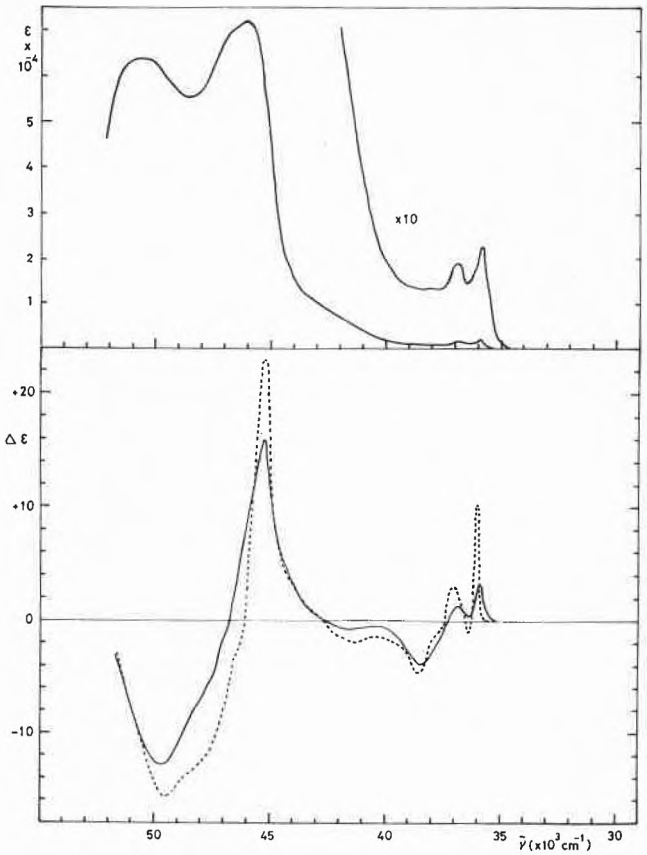

Fig. 2. The UV (top) and CD (bottom) Spectra of (+)-2,7-Dimethyltriptycene; solid lines are at room temperature and a dotted line at low temperature (130 K) in ethanol

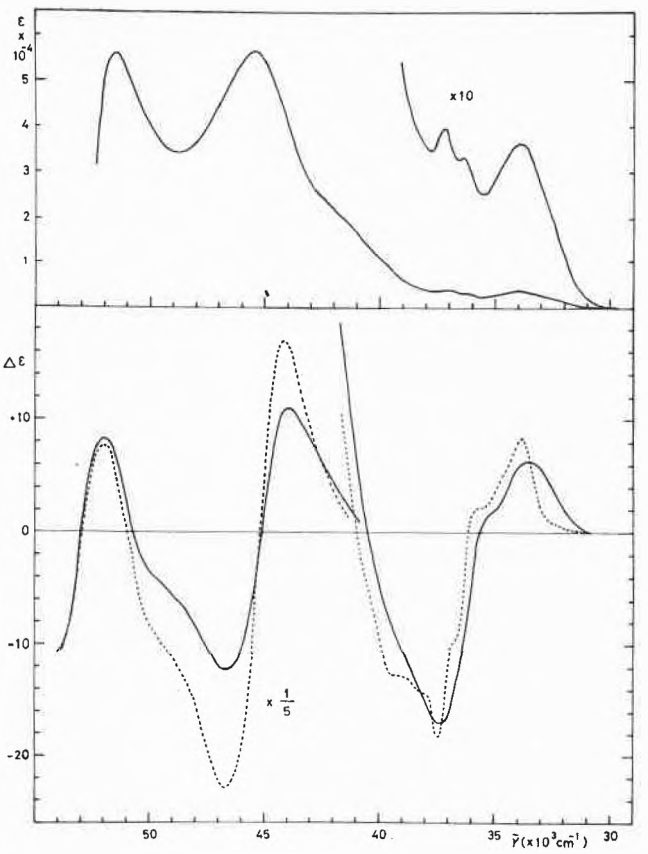

Fig. 3. The UV (top) and CD (bottom) Spectra of (+)-2,7-Diaminotriptycene; solid lines at room temperature and a dotted line at low temperature (130 K)

a view of clarifying the correlation of the spectra and structure and establishing the absolute configuration[1]. The UV and CD spectra of (+)-2,7-disubstituted triptycenes are measured in the 192 $\sim$ 350 nm region, by using a JASCO J-20 spectropolarimeter with a Cryo-Tip refrigerator and a Carl-Zeiss spectrophotometer PMQ II. In Figs. 2 and 3 typical spectra are illustrated on (+)-2,7-dimethyltriptycene (I) and (+)-2,7-diaminotriptycene (II). In the CD spectrum of (I) a sharp positive-negative pair has been found at the lowest energy region.

This band splitting is originated from the degenerate levels of the $^1B_{2u}$ type excited states of methyl-substituted benzene rings, the coupling of the two states will cause a CD band with an opposite rotational strength. In the spectra of (I) the band pair appears with each vibronic levels, thus showing a weak interaction pattern of the exciton splitting. In the spectra of (II) (Fig. 3) a much stronger and broad band pair has been observed, which is an indication of the strong interaction. In the spectral region higher than 44000 cm^{-1} where the $^1E_{1u}$ levels will be expected, the strongest CD band pair has been found on both molecules, and it will be explained by the coupling of the short-axis polarized $^1E_{1u}$ type states. Other 2,7-disubstituted triptycenes show the similar spectral patterns except a few asymmetric bands.

The directions of the polarization of the $^1B_{2u}$ type state and one of the $^1E_{1u}$ state are short-axis, perpendicular to the three-fold symmetry axis of triptycene skeleton. This can be predicted by Platt's rule[2] and has been confirmed by the polarization measurements on the UV spectra of single crystals[3]. The chirality of the coupled chromophore system will be originated in the displacements of the centers of these transition moments as shown in Fig. 1. These shifts can be reasonably explained by the delocalization effect of the π-electrons of the substituent groups and actually is confirmed by a LCAO SCF MO CI calculation on mono-substituted benzenes. Namely the center of the transition moment is placed on the weighted mean of the transition density of the substituted benzene ring, and it is shown that the shift is about 0.3 $\sim$ 0.4 Å towards the substituent for the $^1B_{2u}$ states for most substituted benzenes. For the $^1E_{1u}$ level the shift is about 0.1 Å or less with the same direction of the $^1B_{2u}$ state, though, the strong inductive substituent

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such as fluorine makes a shift into the opposite direction. The displacement of the transition moment is an essential chirality of the present system.

The rotational strength for the coupled chromophore system is evaluated by the standard procedure[4]. The mixing of the excited states of the 2- and 7-substituted benzene rings will cause the lower energy transition with the arrangement of the transition moment as shown in Fig. 1, therefore the appearance of the CD band pair with a lower energy band positive implies that the absolute configuration should be as shown in Fig. 1.

On the other hand the X-ray crystal structure analysis has been performed on (+)-2,5-dimethoxy-7-dimethylaminotriptycene hydrobromide[5], and the absolute configuration is determined by the Bijvoet method. The chemical correlation of the present molecules with (+)-2,5-dimethoxy-7-substituted triptycenes has been carried out[6] and it is found that the absolute configuration determined in this study is not in agreement with the X-ray result. In addition to this we have encountered on several occasions that the rigorous CD spectral analysis of the absolute configuration does not give agreements with the X-ray results[1,7]. Therefore the method of determination of the absolute configuration is examined in detail, and it is found that the theory of the X-ray scattering is not firmly established. Moreover it turns out that the present method of determining the absolute configuration by the X-ray analysis should be changed so as to give the antipodal configuration[8]. It means that the basis of the absolute configuration of the Fischer convention system should be revised to the antipodal configuration.

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Der Lösungsmitteleinfluß auf die UV-Spektren von 1-Alkyl-*s*-triazol-4-N-acyliminen

Summary

The electronic absorption spectra of five 1-alkyl-*s*-triazol-4-N-acylimines have been measured in a number of pure solvents. The hypsochromic shifts are found to be linearly related to the polarity parameters E_T, Z and S. The correlations slopes of these are dependent of the substituents.

Die UV-Absorption dipolarer Verbindungen ist stark vom Lösungsmittel abhängig. Derartige Produkte besitzen eine negative Solvatochromie, d. h. sie absorbieren in einem unpolaren Lösungsmittel längerwellig als in einem polaren[1–6]. Die aus den Absorptionsmaxima errechenbaren molaren Übergangsenergien wurden zum Aufstellen von empirischen Lösungsmittelpolaritätsskalen benutzt (E_T-Werte[1,2] und Z-Werte[7]), die mit Erfolg zur Diskussion verschiedener Lösungsmitteleffekte anwendbar sind. Korrelationen von absorptionsspektroskopischen Daten mit derartigen Parametern in Abhängigkeit von den Substituenten in dipolaren Verbindungen liegen bisher kaum vor. Es wurden deshalb die UV-Spektren von verschiedenen substituierten 1-Alkyl-*s*-triazol-4-N-acyliminen **1a–e**[8] in einigen Lösungsmitteln bestimmt und ihre Beziehungen zu Lösungsmittelparametern geprüft.

[1] C. Reichardt, *Angew. Chem. 77* (1965) 30; *Angew. Chem.* (Internat. Ed.) *4* (1965) 29.
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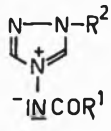
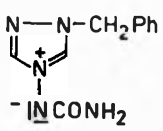
Tabelle 1. UV-Absorptionsmaxima der 1-Alkyl-*s*-triazol-4-N-acylimine **1a–e** und 1-Benzyl-*s*-triazol-4-N-carbamoylimin **2** in verschiedenen Lösungsmitteln (in nm)

Nr.	R^1	R^2	Lösungsmittel						
			H_2O	CH_3OH	C_2H_5OH	CH_3CN	CH_3Cl	CH_2Cl_2	Diox.
1a	H	$PhCH_2$	237	245	252	260	266	268	266
1b	Ph	$PhCH_2$	248	267	270	286	291	296	300
1c	CH_3	$PhCH_2$	237	250	253	263	270	273	281
1d	CH_3	p-$ClC_6H_4CH_2$	235	248	252	264	270	273	270
1e	CH_3	$CH_3(CH_2)_2CH_2$	234	244	247	261	267	267	269
2			246	257	261	272	282		290



1a-e



2

In Tabelle 1 sind die längstwelligen Absorptionsmaxima der N-Imine **1a–e** zusammengestellt*. Da die entsprechenden 1-substituierten *s*-Triazole erst bei wesentlich kürzeren Wellenlängen absorbieren (etwa 210 nm), muß es sich bei dieser Absorption um eine Anregung des π-Systems der acylierten Azomethinimin-Gruppe in den N-Iminen **1a–e** handeln. Durch die elektronische Wechselwirkung zwischen «Überschuß»-Elektronen und den π-Elektronen der Azomethinbindung werden diese leichter angeregt. Daraus resultiert die bathochrome Verschiebung gegenüber den *s*-Triazolen**.

Wie erwartet, zeigt die UV-Absorption der N-Imine **1a–e** und **2** eine negative Solvatochromie. Mit Ausnahme einiger in Dioxan gemessener Werte korrelieren die aus den Absorptionsfrequenzen berechneten molaren Übergangsenergien sehr gut mit den E_T-Werten nach der allgemeinen Beziehung

$$E'_T = aE_T + b,$$

vgl. Tabelle 2 und Abb. 1.

Die mit Hilfe einer Ausgleichsrechnung ermittelten Parameter a und b dieser Geradengleichung enthält

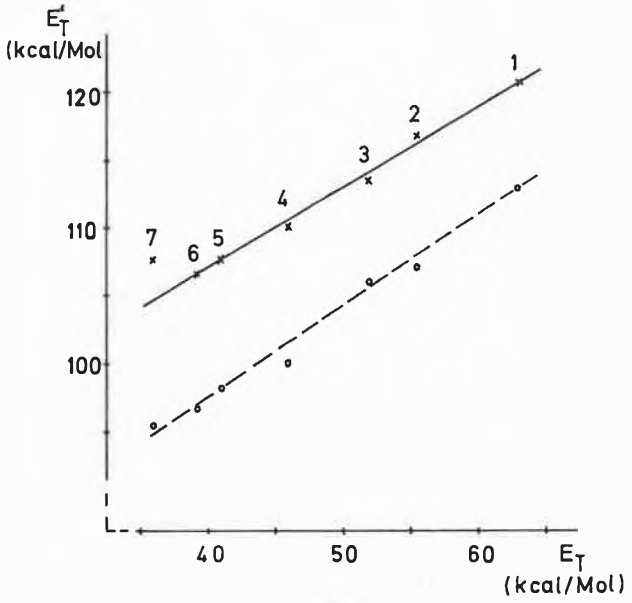


Abb. 1. Beziehungen zwischen E_T/E'_T-Werten für 1-Benzyl-*s*-triazol-4-N-formylimin **1a** (——) und 1-Benzyl-*s*-triazol-4-N-benzoylimin **1b** (– – – –). 1 Wasser, 2 Methanol, 3 Äthanol, 4 Acetonitril, 5 Methylenchlorid, 6 Chloroform, 7 Dioxan

* Die Tabellen 1 und 2 enthalten auch die Daten für das 1-Benzyl-*s*-triazol-4-N-carbamoylimin **2**, die wir schon an anderer Stelle veröffentlicht haben[9].

** Eine derartige langwellige Absorption ist charakteristisch für Amin-N-imine, vgl. Übersicht[11].

Tabelle 2. Korrelation zwischen E_T-, E'_T- und *S*-Werten für 1-Alkyl-*s*-triazol-4-N-acylimine **1a–e** und 1-Benzyl-*s*-triazol-4-N-carbamoylimin **2**

Nr.	*a*	*b*	*s*	*r*	R-Konstante	*r*
1a	0,54	86,0	1,2	0,980	0,1487	0,997
1b	0,72	68,3	1,2	0,988	0,1887	0,978
1c	0,67	78,2	0,5	0,997	0,1638	0,995
1d	0,62	80,2	1,5	0,977	0,1743	0,996
1e	0,63	82,3	1,1	0,986	0,1670	0,995
2	0,68	73,8	0,6	0,997	0,1710	0,999

a = Anstieg der Regressionsgerade E'_T/E_T, b = Ordinatenabschnitt (kcal/Mol), s = Standardabweichung von b (kcal/Mol), r = Korrelationskoeffizient

Tabelle 2. Von diesen beiden Parametern gibt der Wert a die Lösungsmittelsuszeptibilität des UV-Überganges an. Wie aus Tabelle 2 folgt, ist die Größe von a sowohl von den Substituenten in 1-Stellung des *s*-Triazolringes als auch von denen der Acyliminogruppe abhängig. Wird die Formylverbindung **1a** als Bezugssubstanz festgelegt, dann besitzen alle in 4-Stellung verschieden substituierten N-Imine mit gleichem Substituenten am N-1-Atom einen höheren a-Wert. Diese Änderungen sind größer als bei den N-Acetyliminen **1c–e** mit unterschiedlichen Resten in 1-Stellung. Das läßt auf eine stärkere Wechselwirkung der *exo*-N-Substituenten mit dem Azomethinimin-System in den N-Iminen **1** und **2** schließen. Mit Hilfe der Substituenten R^1 und R^2 in den Verbindungen **1** und **2** ist es nicht sinnvoll, quantitative Aussagen über die Abhängigkeit des a-Wertes von Substituentenkonstanten zu treffen. Derartige Korrelationen sind bei geeigneten Substituenten auf jeden Fall zu erwarten. Qualitativ läßt sich die Beeinflussung des a-Wertes der Verbindungen **1** und **2** mit den normalen elektronischen Effekten erklären.

Die Substituentenwirkung wird ebenfalls aus den R-Werten der freien linearen Energiebeziehung für Lösungsmittelparameter nach BROWNSTEIN[10] deutlich, vgl. Tabelle 2. Allerdings ändern sich auch in diesem Falle die Werte zwischen den einzelnen Verbindungen nicht sehr gravierend. Dazu fehlen offenbar stärkere mesomere Wechselwirkungen der Substituenten. Da zwischen den *Z*-Werten nach KOSOWER[7] und den E_T-Werten eine lineare Korrelation besteht ($Z = 1{,}411\ E_T + 6{,}92$), ist eine derartige Beziehung auch zwischen den E'_T-Werten der Verbindungen **1a–e** sowie **2** und den *Z*-Werten vorhanden. Wie erwartet, gibt es dagegen zwischen E'_T und den Dielektrizitätskonstanten, der KIRKWOOD-Konstante K und den δ-Werten[3] keine Korrelation.

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