

deficiencies in the description of sterically strained π systems (see ref.^[16] and references cited therein). Indigo itself has been studied by Hückel molecular orbital (MO) and PPP methods^[17], but no study of the isomerization reaction using semiempirical valence-electron MO methods has been reported so far.

Previous experience with substituted polycyclic aromatic hydrocarbons has shown that MO calculations based on the AM1 Hamiltonian give encouraging results for large organic π systems incorporating strong steric interactions^[16]. In this paper we report on AM1-SCF^[18] (self-consistent field) calculations of the ground-state structures of the *cis* and *trans* isomers of indigo (**1** and **2**) and *N,N'*-diacetylindigo (**3** and **4**). We used these molecules as model compounds to improve our understanding of the isomerization reaction of large organic dyes on a structural basis. To test the reliability of the method we also performed an X-ray diffraction study of **3** to compare experimental and calculated geometrical parameters. Moreover, the potential energy curves (PEC) for the *cis* \rightarrow *trans* isomerization reaction **2** \rightarrow **1** and **4** \rightarrow **3** in several electronic states were calculated with the AM1 method including configuration interaction (CI). The calculated enthalpies of activation (ΔH^\ddagger) for the thermal (back)isomerization process of the *cis* isomers in the ground state are compared with experimental data to assess the performance of the AM1-CI method. The ΔH^\ddagger values are of particular importance for the reversibility of the information storage cycle using PLCs.

The photochemical behaviour of indigo dyes is discussed qualitatively by using the calculated PECs of the T_1 - and S_1 -excited states. The calculational results should enable us (a) to predict the thermal stability of photochemically generated *cis* isomers with similar structure as yet unknown and (b) to obtain information on the correlation between the curvature of the excited state PECs and the photoisomerization capability. Our discussion centres on the results for the *N,N'*-diacetylindigo dyes and includes the parent compounds *cis*- and *trans*-indigo for comparison.

Results and Discussion

Geometries and Energies

Because of strong steric interactions between the acetyl group and the carbonyl group (in the *trans* form) and between the acetyl groups themselves (in the *cis* form) we investigated three rotational conformers of **3** and **4** (see Scheme 2).

These rotational conformers differ in the relative orientation of the acetyl groups with respect to the carbonyl group of the five-membered ring or to the neighbouring acetyl group. All structures were fully optimized at the AM1-SCF level without any symmetry restrictions. The structures obtained all represent minima on the *N,N'*-diacetylindigo hypersurface as found by subsequent vibrational analysis (all vibrational frequencies are real). The relative energies of the various isomers/conformers (see Table 1) are discussed first.

The most stable isomer is the *trans* form **3a** with two methyl/carbonyl-group interactions (see also Scheme 2) on both sides of the molecule. Conformer **3b** is only slightly

higher in energy with a methyl/carbonyl and a carbonyl/carbonyl interaction. Inspection of Table 1 shows that there is a rough correlation of the *trans*-conformer stability with the deformation angle β . This angle measures the torsion of the plane of the acetyl group with respect to the indoxyl moiety (dihedral angle C8–N1–C11–O12) and thus gives an indication of the strength of the steric interactions. The close proximity of the two carbonyl groups in **3b** and **3c** seems to be the most unfavourable due to the electrostatic repulsion of the negatively charged oxygen atoms which are separated by only 265 pm (in **3c**).

Scheme 2

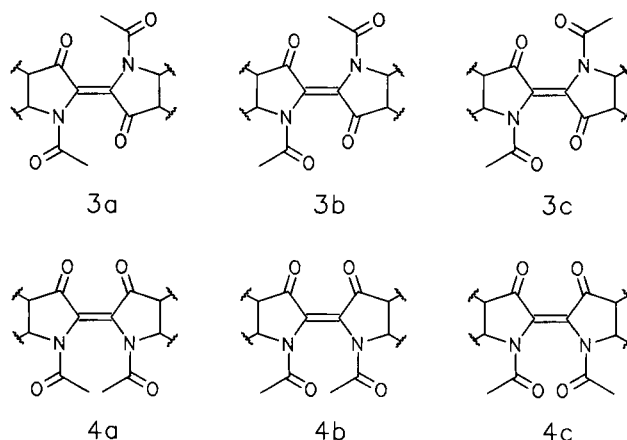


Table 1. Relative energies^[a] $\Delta\Delta H_f^\ddagger$ and deformation angles Θ , α and β of *cis*- and *trans*-*N,N'*-diacetylindigos **3a–4c** obtained with the AM1-SCF method; experimental values from the X-ray diffraction analysis are given in parentheses^[b]

Compound	$\Delta\Delta H_f^\ddagger$ [kcal/mol]	Θ [°] [°]	α [°] [°]	β [°]
<i>trans</i> form				
3a	0.0	32.5 (42.4)	13.0 (19.6 ^[e])	32.0 (28.5 ^[f])
3b	0.1	24.3	10.5	50.5
3c	1.5	18.7	8.5	56.1
<i>cis</i> form				
4a	1.2	23.1	11.3	40.9
4b	3.1	22.7	10.2	47.0
4c	3.9	23.1	9.0	35.5

^[a] Difference in the heat of formation with respect to **3a** [ΔH_f^\ddagger (**3a**) = -5.4 kcal/mol]. - ^[b] The deformation angles α and β of the experimental structure refer to the average values from both sides of the molecule. - ^[c] Given as $180 - \Theta$. - ^[d] Given as $180 - |\alpha|$. - ^[e] $\alpha(\text{C2}-\text{C2}'-\text{C3}'-\text{N1}') = 17.7^\circ$; $\alpha(\text{C2}'-\text{C2}-\text{C3}-\text{N1}) = 21.4^\circ$. - ^[f] $\beta(\text{C8}-\text{N1}-\text{C11}-\text{O12}) = 23.1^\circ$; $\beta(\text{C8}'-\text{N1}'-\text{C11}'-\text{O12}') = 33.9^\circ$.

A similar situation is found for the *cis* conformers **4a–c**, where the separation of the oxygen atoms of the five-membered ring carbonyl groups is slightly lower (240–245 pm in **4a–c**, respectively). These compounds are generally higher in energy than the most stable *trans* isomer, but the energy gap [*trans* versus *cis*, $\Delta\Delta H_f^\ddagger = \Delta H_f^\ddagger$ (*trans*) - ΔH_f^\ddagger (*cis*)] is lower as compared to the parent molecule indigo (AM1-SCF: $\Delta\Delta H_f^\ddagger = -7.1$ kcal/mol). This is easily explained

by the existence of the bridging NH...OC hydrogen bond in **1**, which stabilizes the *trans* but not the *cis* isomer.

Inspection of the relative stabilities of the conformers of **4** confirms the explanation given above for the energetic ordering of the conformers of **3**. The most stable structure **4a** has the methyl/methyl arrangement while **4c** (two carbonyl/carbonyl interactions) is highest in energy. The relative stabilities of the three *cis* isomers as obtained with the AM1 method are exactly reversed compared to the results of the MNDO study of Takahashi et al.^[15], where **4c** was found to be most stable [ΔH_f^0 (**4a**) - ΔH_f^0 (**4c**) = 2.2 kcal/mol]^[15]. We believe that the MNDO results are incorrect, since it is well-known that the parametrization of the core-core repulsion function in MNDO tends to overestimate atomic repulsions near the van der Waals distance^[18]. Such situations apparently arise in **4** from the close proximity of the two acetyl and carbonyl groups.

The inclusion of electron correlation at the SD-CI level of theory does not alter the ordering of relative stabilities, although the energy gap between **3a** and **3b** is increased to 0.4 kcal/mol. The experimental reaction enthalpy for **4** → **3** ($\Delta H_R = -8.1$ kcal/mol^[11]), which is probably an average value for all conformers studied here, is lower than our calculated values of -1.2 to -3.0 kcal/mol (see Table 4). Considering the usually large deviations of different experimental values (several kcal/mol, cf. the analogous data e.g. of stilbene^[22]) this difference does not seem alarming. Moreover, deviations of several kcal/mol between calculated (gas

phase) and experimental (liquid phase) heats of isomerization are to be expected.

The heavy-atom skeleton of indigo itself in the *trans* form is calculated to be nearly planar (Θ and α are less than 2°). However, there is a slight pyramidalization of the nitrogen atoms (ca. 7°) and a strong out-of-plane bending of the hydrogen atoms connected with them (ca. 25°). The former finding is in agreement with experimental X-ray data of indigo^[23]. The *cis* isomer of indigo, however, shows a very shallow potential energy curve (PEC) for the torsion of the C-C double bond with a minimum at $\Theta \approx 25^\circ$ demonstrating the unfavourable proximity of the two carbonyl groups.

The calculated geometries of the *N,N'*-diacetylindigos all have a nonplanar indigo moiety, whereas the two indoxyl parts of the molecules are nearly planar. We use the deformation angles Θ and α (see Figure 1) to describe the torsion around the central C-C double bond (Θ) and the pyramidalization (α) at the carbon atoms C2 and C2'. Following the natural choice of Θ as a reaction coordinate in the calculation of the isomerization reaction pathways, we have used the simple dihedral angles in the description of the nonplanar indigo moiety. Lüttke et al.^[14] used a different

Table 2. Comparison of calculated (AM1-SCF) and experimental^[a] bond lengths [pm] and bond angles [°] of indigo (**1**) and *trans,N,N'*-diacetylindigo (**3a**); the numbering of the atoms refers to Figure 1

Parameter	1		3a	
	Calc.	Exp. ^[b]	Calc.	Exp. (this work)
bond lengths				
C2-C2'	135.7	137	136.2	134.9
C2-C3	151.5	148	152.4	149.7
C2-N1	141.7	136	142.8	141.4
C3-O10	122.9	122	122.7	121.7
C3-C9	147.6	147	147.4	146.5
N1-C8	141.0	138	142.9	142.5
N1-C11	-	-	141.6	141.2
C11-O12	-	-	124.1	120.7
C11-C13	-	-	150.3	149.0
benzene ring	138.3-140.0	137-138	138.3-140.0	137.4-139.4
bond angles				
C2-N1-C8	107.8	109	107.5	107.9
N1-C8-C9	110.7	109	110.6	110.0
C3-C9-C8	107.6	107	108.1	109.1
C2-C3-C9	104.2	105	104.3	104.2
N1-C2-C3	108.9	109	108.5	107.7
C2'-C2-C3	125.8	126	124.6	125.0
C2'-C2-N1	125.3	125	125.6	124.1
C2-C3-O10	125.6	126	126.7	126.5
O10-C3-C9	130.1	129	128.9	129.0
C2-N1-C11	-	-	125.6	127.0
C8-N1-C11	-	-	120.7	121.8
N1-C11-O12	-	-	118.5	119.1
N1-C11-C13	-	-	120.4	118.2
O12-C11-C13	-	-	121.0	122.5
benzene ring	117.8-121.8	118-122	117.8-121.8	117.1-122.3

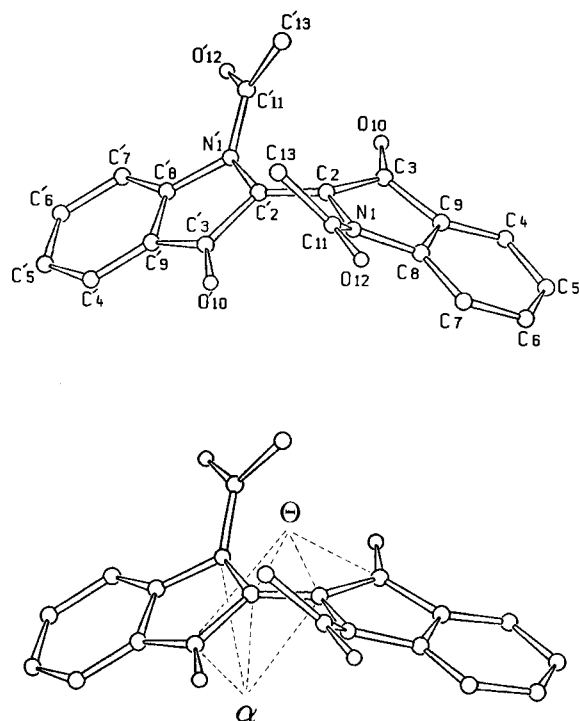


Figure 1. Comparison of the molecular structure of **3a** (hydrogen atoms omitted) obtained by X-ray diffraction (top) and AM1-SCF optimization (bottom), the torsion angle Θ and the pyramidalization angle α (the sequence is C2-C2'-C3'-N1' and C2'-C2-C3-N1, respectively) used in the description of the deformation of the indigo moiety are indicated in the AM1 structure

^[a] The bond lengths and bond angles of the experimental structure **3a** refer to the average values from both sides of the molecule. The average standard deviation of bond lengths (bond angles) is 0.5 pm (0.4°). — ^[b] Ref.^[23].

Table 3. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{pm}^2 \times 10^{-1}$) for compound **3a**

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq)
N1	6984(2)	4523(3)	6362(2)	24.8(12)
C2	7252(3)	3632(4)	5678(2)	24.4(12)
C3	6360(3)	2490(4)	5199(3)	26.4(13)
C4	4555(3)	2242(4)	5387(3)	30.8(13)
C5	3957(3)	2785(5)	5894(3)	34.1(15)
C6	4339(3)	4013(5)	6562(3)	33.7(14)
C7	5321(3)	4710(5)	6753(3)	30.5(14)
C8	5926(3)	4121(4)	6252(3)	25.4(11)
C9	5543(3)	2913(4)	5574(3)	26.8(12)
O10	6324(2)	1499(3)	4590(2)	33(2)
C11	7690(3)	5268(4)	7220(3)	29(2)
O12	7346(2)	6188(3)	7647(2)	43(2)
C13	8827(3)	4763(5)	7607(3)	39(2)
N1'	8221(2)	3175(3)	4609(2)	25(2)
C2'	7998(3)	4050(4)	5326(2)	24.5(14)
C3'	8388(3)	5701(4)	5320(3)	27(2)
C4'	8842(3)	7054(4)	3954(3)	31(2)
C5'	8928(3)	6821(5)	3061(3)	36(2)
C6'	8799(3)	5318(5)	2649(3)	33(2)
C7'	8596(3)	4016(5)	3117(3)	31(2)
C8'	8493(3)	4268(4)	4006(3)	24(2)
C9'	8611(3)	5761(4)	4418(3)	26(2)
O10'	8392(2)	6760(3)	5878(2)	33(2)
C11'	8506(3)	1569(4)	4661(3)	28(2)
O12'	8682(2)	988(3)	3985(2)	40(2)
C13'	8646(3)	679(4)	5573(3)	34(2)

definition of these deformation angles to describe the (non-planar) structure of *N,N'*-dimethylindigo^[*]. These torsions essentially reduce the steric strain in **3** and **4**. The geometries of these compounds will be discussed in more detail.

The calculated structures of the *trans* isomers exhibit a "U-shaped" arrangement of the two indoxyl moieties (i.e. the pyramidalization at C2 and C2' occurs in the same direction) while the *cis* isomers have a "chair" conformation with $\alpha(\text{C}2') = 180 - \alpha(\text{C}2)$. The molecular geometries (without the acetyl groups) deviate only slightly from C_2 symmetry with the twofold axis either perpendicular to the N1'–C2'–C2–N1 plane (*trans* forms) or parallel to it (perpendicular to the C2'–C2 axis, *cis* forms). The torsion angles Θ are generally larger (by a factor of two) than the pyramidalization angles. Inspection of the data for **3a–c** in Table 1 shows that Θ and α decrease with increasing β , i.e. a strong out-of plane arrangement of the acetyl groups is compensated by a smaller deformation of the indigo moiety. Thus, we can conclude that the force constants for the respective torsions are of equal magnitude. Interestingly, the most stable conformer **3a** exhibits the largest values for the angles Θ and α . This demonstrates furthermore that the deformation of the conjugated π system in these molecules is not an exclusive criterion for energetic stability.

[*] Our experimental values for the twisting and pyramidalization angles, as defined by Lüttke et al., for **3a** are 37.9° , 17.5° (C2') and 30.1° (C2), respectively. The comparison with the corresponding values of *N,N'*-dimethylindigo (26 and 9.5°) shows that the steric strain induced by the substituents is significantly larger for acetyl than for methyl groups.

The structure of *N,N'*-diacetylindigo as obtained from our X-ray diffraction work has the *trans* configuration (see Figure 1 and 2). The structure is "U-shaped" and is identified as the rotational conformer **3a** with two methyl/carbonyl interactions. This finding corresponds nicely with the theoretical prediction since **3a** is most stable at the AM1-SCF and AM1-SDCI theoretical levels. The agreement between calculated and experimental structural data is quite satisfactory (see Figure 1 and Table 1 and 2) by considering the complicated intramolecular interactions. Compared to the X-ray data the calculated bond lengths are generally longer by 1–2 pm. The comparison of the calculated and the experimental structure in Figure 1 shows clearly that the latter geometry is significantly distorted from C_2 symmetry [$\alpha(\text{C}2) = 21.4^\circ$, $\alpha(\text{C}2') = 17.7^\circ$]. This may be attributed to the packing forces in the crystal of **3a** and explains the lower value of Θ and α of the AM1-optimized structure.

As suggested by one referee we have performed SCF optimizations of **3a–4c** with the PM3 Hamiltonian^[26], which is a reparametrized version of the MNDO method. With PM3 we have found the reverse (wrong) ordering of the relative stabilities of the various conformers, i.e. **3c** becomes most stable at the PM3 level. The results for the *cis* \rightarrow *trans* isomerization enthalpies for **4** \rightarrow **3** are very similar to the AM1 values [PM3: $\Delta H_R = -2.5$ (a), -2.8 (b) and -0.5 kcal/mol (c)]. The calculated geometry of **3a** shows significant deviations compared to the AM1 and the X-ray structure in the C–N bond lengths (which are too long by 3–4 pm), in a much larger out-of-plane torsion of the acetyl groups (PM3: $\beta = 48^\circ$; AM1: $\beta = 32^\circ$; X-ray: $\beta = 28.5^\circ$) and in a too strong pyramidalization at the nitrogen atoms (PM3: 40° ; AM1: 26° ; X-ray: 20°). Obviously, the PM3 method gives no improvement over MNDO for these compounds.

Finally, it is noted that the observed structure of *N,N'*-diacetylindigo is very similar to the structure of *N,N'*-dimethylindigo reported by Lüttke et al.^[14]. The AM1-SCF results for *N,N'*-dimethylindigo (not shown) also compare very well with the experimental data, and we conclude that AM1 is the method of choice for the description of structural and energetic ground-state data of sterically crowded indigo dyes.

Isomerization Reaction

The activation enthalpy (ΔH^\ddagger) for the thermal *cis* \rightarrow *trans* isomerization of *N,N'*-diacetylindigo in the ground state has been determined experimentally by Paetzold et al.^[24] and Weiss et al.^[25]. The values of 18.1 kcal/mol and 23.1 kcal/mol are much lower than the analogous values observed for the isomerization reactions of other olefins [e.g. ΔH^\ddagger (ethene) = 65 kcal/mol; ΔH^\ddagger (stilbene) = 46 kcal/mol; see ref.^[18,22] and references cited therein]. A simple theoretical approach for calculating the ground-state barriers is a correlation of the ΔH^\ddagger values with the π -bond order p_π . This correlation for the values for the compounds given above is significant [AM1-SCF: $p_\pi(\mathbf{1}) = 0.72$; $p_\pi(\mathbf{3a}) = 0.76$; $p_\pi(\text{stilbene}) = 0.87$; $p_\pi(\text{ethene}) = 1$] and suggests the usage of the p_π values as a first estimate of the isomerization barrier.

Generally, the isomerization reaction around a C–C double bond proceeds along a diradicaloid intermediate at a torsion angle of $\Theta \approx 90^\circ$. The diradicaloid (rather than dipolar) nature of this intermediate in the case of *N,N'*-diacetylindigo has been inferred from solvent variation by Nishimura et al.^[13] The SCF-based single-determinant approach inherently cannot describe such a situation, and thus configuration interaction (CI) methods must be included (compare for example the ab initio calculations of ethene^[27]).

The AM1-SDCI results for the *cis* → *trans* isomerization barriers ΔH^\ddagger of the *N,N'*-diacetylindigo conformers are summarized in Table 4. The potential energy curves (PEC) of the S_0 , T_1 , S_1 and S_2 states calculated for the isomerization reaction of the *N,N'*-diacetylindigo are shown as an example for the most stable conformer **a** in Figure 2. It is important to mention that the relative orientation of the acetyl groups is preserved during the reaction pathway (optimization process). Thus, a direct relation exists between the conformers **a**–**c** of the *cis* and *trans* isomers (see Scheme 2) and a one-dimensional description of the isomerization reaction seems appropriate.

Table 4. Comparison of calculated^[a] (AM1-SDCI^[b], SCF values in parentheses) and experimental enthalpies of activation (ΔH^\ddagger) for the thermal *cis* → *trans* isomerization of indigo and *N,N'*-diacetylindigos in the ground state; ΔH_R is the reaction enthalpy for the *cis* → *trans* isomerization reaction at the AM1-SCF level

Reaction	ΔH_R [kcal/mol]	ΔH^\ddagger [e] [kcal/mol]
AM1		
2→1	-7.1 [d]	24.6 (33.5)
4a→3a	-1.2	21.9 (30.1)
4b→3b	-3.0	20.5 (28.6)
4c→3c	-2.2	20.4 (28.5)
Exp.		
4→3	-8.1 [e]	18.1 [f] / 23.1 [g]

[a] The data given refer to the maximum of the potential energy curve obtained from a cubic spline interpolation of 12–15 data points. — [b] 30 valence electrons of the occupied MOs with the highest orbital energies were correlated. — [c] $\Delta H^\ddagger = E_a - RT$. — [d] $\Delta H^\ddagger = 38.9$ kcal/mol. — [e] Ref.^[11]. — [f] Ref.^[24]. — [g] Ref.^[25].

The ground-state (S_0) PEC is nearly symmetrical and exhibits a maximum at $\Theta = 90^\circ$. The enthalpy difference between the minimum of the *cis* isomer and the maximum is calculated to be 21.9 kcal/mol at the SDCI level and 30.1 kcal/mol at the SCF level (the SCF PEC is not shown). The corresponding ΔH^\ddagger values for the reactions of the conformers **b** and **c** are only slightly lower (see Table 4). The agreement between the calculated (AM1-SDCI) and the experimental values is excellent, which demonstrates the applicability of the theoretical model. The SCF approximation overestimates ΔH^\ddagger by ca. 8 kcal/mol due to the neglect of electron correlation, which is most important for the diradicaloid structure at $\Theta = 90^\circ$ (strong admixture of a doubly excited HOMO → LUMO configuration). A comparison with data for the parent compound indigo (ΔH^\ddagger is larger

by 2–4 kcal/mol; see Table 4) shows that no correlation of ΔH^\ddagger with the reaction enthalpy ΔH_R (Hammond postulate) can be found. In Figure 3 the ground-state PECs of indigo and *N,N'*-diacetylindigo (**a**) normalized to equal height at $\Theta = 90^\circ$ are shown. Comparison of these curves shows that, relative to indigo, only the *trans* isomer **3a** is destabilized by the steric effect of the substituents while the *cis* isomers are nearly equal in relative energy. This analysis explains the similarity of the calculated ΔH^\ddagger values for **2** and **4**. The similar shape of both PECs in the range $\Theta = 50 - 130^\circ$ indicates that electronic effects (induced by the acetyl groups) on the height of the barrier are negligible. Moreover, our results predict that the (experimentally unknown) *cis* isomer of indigo should be relatively stable to thermal back-isomerization and, once formed, should be isolable.

The photoisomerization reaction *trans* → *cis* of **3** has been investigated by applying direct excitation and under triplet-sensitized conditions^[2,8,9,28,29]. The proposed reaction from

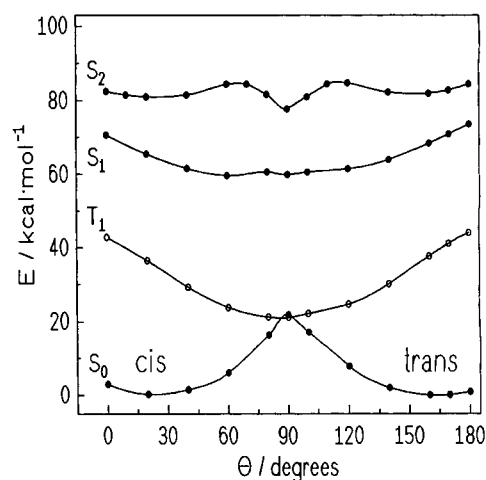


Figure 2. AM1-SDCI energies of the four lowest states S_0 , T_1 , S_1 and S_2 of *N,N'*-diacetylindigo (**a**) as a function of the torsion angle Θ [°] of the central C–C double bond; the energies are given relative to the minimum of the S_0 curve of **4a** at 20°

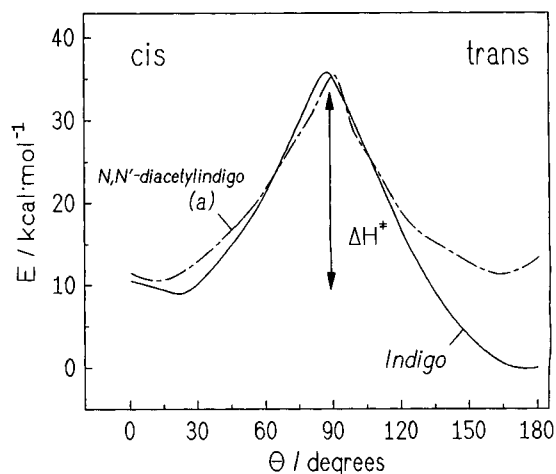


Figure 3. AM1-SDCI energies of the ground states of indigo and *N,N'*-diacetylindigo as a function of the torsion angle Θ [°] of the central C–C double bond; the energies are normalized to equal height of the maxima

the S_1 state has been confirmed experimentally, whereas a participation of the T_1 state in the photoisomerization reaction is still questionable^[29].

Inspection of Figure 2 shows that the PECs of the S_1 and T_1 states have minima at the diradicaloid geometry. Starting from a vertically excited Franck-Condon state of the *cis* or the *trans* isomer the energy drops steadily as Θ approaches 90° . Contrary to the case of stilbene^[22] or ethene^[27] no barrier to the isomerization process in the S_1 state is found. The S_1 and T_1 states are mainly described by a singly excited HOMO \rightarrow LUMO configuration while the S_2 state wave function becomes dominantly doubly excited (HOMO \rightarrow LUMO) at $\Theta = 90^\circ$. Therefore, the missing barrier can be explained by the high energy of the S_2 state which cannot give rise to an avoided crossing in the critical part of the PEC. Thus, from the curvature of the S_1 -state PEC we can deduce a fast isomerization reaction which is indeed found experimentally (barrier < 1 kcal/mol; $k_{\text{iso}} = 1.2 \cdot 10^8 \text{ s}^{-1}$)^[29]. The reliability of these results is further demonstrated by the comparison of the calculated and experimental excited-state energies ΔE .

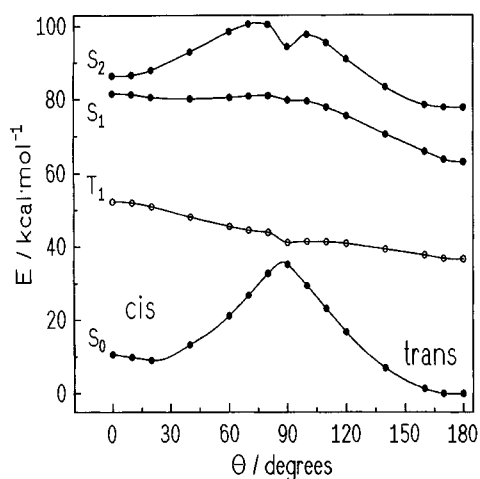


Figure 4. AM1-SDCI energies of the four lowest states S_0 , T_1 , S_1 and S_2 of indigo as a function of the torsion angle Θ [$^\circ$] of the central C-C double bond; the energies are given relative to the minimum of the S_0 curve of indigo at ca. 178°

The vertical excitation energy of the S_1 state of the *trans* form **3a** ($\Delta E_{\text{calcd.}} = 2.9$ eV; $\Delta E_{\text{exp.}} = 2.2$ eV^[5]) is overestimated by ca. 0.7 eV while the T_1 energy is approximately correct ($\Delta E_{\text{calcd.}} = 1.7$ eV; $\Delta E_{\text{exp.}} \approx 1.7$ eV^[28]). However, the hypsochromic shift of the S_1 -state energy upon *trans* \rightarrow *cis* isomerization ($\Delta\Delta E_{\text{calcd.}} = 0.3$ eV; $\Delta\Delta E_{\text{exp.}} = 0.6$ eV^[5]) is correctly obtained with the AM1-SDCI method. The calculated hypsochromic shift of the S_1 -state energy in going from indigo to *N,N'*-diacetylindigo is also in reasonable agreement with the experimental data ($\Delta\Delta E_{\text{calcd.}} = 0.1$ eV; $\Delta\Delta E_{\text{exp.}} = 0.15$ eV^[5]). This shift is mainly attributed to the electron-withdrawing effect of the acetyl groups, which overcompensates the influence of the twisted and pyramidalized indoxyl moieties (expected as bathochromic shift because of the lowering of the HOMO-LUMO energy gap, see also ref.^[14]). The excitation energies reported here compare better

(by ca. 0.2 eV) with experimental data than the previous MNDO results reported by Takahashi et al.^[15].

A comparison of the calculated PECs of *N,N'*-diacetylindigo with those of the parent molecule indigo demonstrates significant changes in the photochemical behaviour. This is in agreement with experimental observations. The energies of the S_1 and T_1 states of indigo (see Figure 4) increase steadily along the *trans* \rightarrow *cis* isomerization pathway. Neither curve shows a distinct minimum at $\Theta = 90^\circ$, and significant barriers to the isomerization process in the excited states are expected. This contrasting behaviour suggests the energetic importance of the bridging $\text{NH}\cdots\text{OC}$ bonds in the excited states, which is also seen by the increased negative partial charge q at the oxygen atoms O10 and O10' upon excitation to the S_1 or T_1 state [$q_0(S_0) = -0.29$; $q_0(T_1) = -0.33$; $q_0(S_1) = -0.34$]. The CI calculations suggest an explanation for the photostability of indigo without using the hypothesis of a full proton transfer in the excited state. Since the validity of this mechanism is not clear at present (although the increased basicity of the carbonyl groups seem to support this view), further theoretical work is in progress.

Conclusions

The design of new organic dyes for applications in information and energy storage is an important object of future chemical research. Our work shows that the AM1-SCF method can be successfully employed to calculate ground-state data of dyes like indigo. Including configuration interaction (at the relatively cheap SD-CI level), we successfully calculated (relative) excited-state energies, potential-energy curves for the (photo)isomerization reaction and the thermal stability of photochemically generated *cis* isomers. Neither simple π -electron models such as HMO and PPP (neglect of the σ -electron framework) nor much more sophisticated ab initio treatments (due to the size of the molecules) are capable of this task.

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Methods

Theoretical: The semiempirical AM1 calculations were performed with the MOPAC 5.0 program system^[19], which was modified to allow subsequent CI calculations. The geometry optimizations were performed at the SCF level by using internal coordinates. All energy minima were optimized with a precision of better than 0.1 kcal/mol (norm of gradient $< 0.5 \text{ kcal} \cdot \text{mol}^{-1} \cdot \text{\AA}^{-1}$). The geometries along the reaction path for the twisting motion around the central C-C double bond were also calculated at the SCF level by assuming the dihedral angle C3-C2-C2'-C3' (Θ ; see Figure 1) as a reaction coordinate ($0-180^\circ$). The pyramidalization angles α (dihedral angles C2-C2'-C3'-N1' and C2'-C2-C3-N1) were kept fixed at the optimum values of the *cis* isomer while all other geometrical variables were fully optimized. Subsequent single-point CI calculations including spin-adapted singly and doubly excited configura-

rations (SD) with respect to the closed-shell Hartree-Fock (HF) determinant were carried out as described in ref.^[20].

Crystal Structure Analysis of Compound 3a

Synthesis: *N,N'*-diacetylindigo (3) was prepared according to the method of Blanc and Ross^[21], and the crystals for the X-ray studies were grown in a mixture of ether and dichloromethane.

Crystal data: C₂₀H₁₄N₂O₄; *M* = 346.3; monoclinic; space group *P*2₁/*n*; *a* = 1358.7(3), *b* = 848.6(2), *c* = 1471.2(4) pm; β = 112.31(3)°; *V* = 1.5693 nm³; *Z* = 4, *D*_x = 1.466 Mg m⁻³; λ(Mo-K_α) = 71.069 pm; μ = 0.10 mm⁻¹; *F*(000) = 720; *T* = -95°C.

Data collection and reduction: Data were collected from a red tablet ca. 0.45 × 0.25 × 0.1 mm, which was mounted on a glass fibre with inert oil and transferred to the cold gas stream of the diffractometer (Stoe STADI-4 with modified Siemens LT-2 low-temperature attachment). 4943 intensities were registered to 2Θ_{max} = 55°, of which 3582 were independent. Cell constants were refined from ±ω angles of 48 reflections in the 2Θ range of 20–24°.

Structure solution and refinement: The program system SHELXS/SHELXL (G. M. Sheldrick, unpublished) was used. The structure was solved with direct methods and refined anisotropically on *F*². H atoms were included by using a riding model. The weighting scheme was $w^{-1} = \sigma^2(F_o^2) + (0.0319 P)^2 + 2.2155 P$, where $3P = F_o^2 + 2F_c^2$. The final *R*(*F*²) value for all reflections was 0.184, with a conventional *R*(*F*) value of 0.076 for 2075 reflections > 4σ(*F*). 237 parameters, 237 restraints on displacement parameters: *S* = 1.1; max. Δ/σ = 0.015; max. Δρ = 0.3 · 10⁻⁶ e pm⁻³. Further details of the crystal structure investigation are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, W-7514 Eggenstein-Leopoldshafen 2, F.R.G., on quoting the depository number CSD-56884, the names of the authors, and the journal citation.

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