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Photoelectron and UV Spectroscopic Investigations of Homoconjugative Interactions between Parallel C=C and N=N Bonds[1)]

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The photoelectron and UV spectra of diazaisodrin systems **4** and **5** have been measured and analyzed. The strong homoconjugative interaction between the C=C and N=N bond is reflected in a particular destabilized position of the norbornene type π orbital. The UV spectra have been assigned using a CNDO-CI treatment and excellent agreement between observed and calculated values has been achieved. The transanular $\pi_- \rightarrow \pi_-^*$ transition which is not discernible in the parent hydrocarbon can easily be identified in the diaza derivative. X-ray structure determination of **4a** and **5a** confirms the conclusions arrived at by semiempirical calculations.

Photoelektronen- und UV-spektroskopische Untersuchungen zur Homokonjugation zwischen parallelen C=C- und N=N-Bindungen[1)]

Die Photoelektronen- und UV-Spektren von Diazaisodrinen **4** und **5** wurden gemessen und analysiert. Die beträchtliche Homokonjugation zwischen C=C- und N=N-Bindungen spiegelt sich in einem deutlich destabilisierten π-Orbital vom Norbornentyp wider. Die UV-Spektren wurden mit Hilfe der CNDO-CI-Methode interpretiert, und es ergab sich eine ausgezeichnete Übereinstimmung zwischen beobachteten und berechneten Werten. Der transanulare $\pi_- \rightarrow \pi_-^*$-Übergang, der im Stammkohlenwasserstoff nicht erkennbar ist, läßt sich im Diazaderivat leicht identifizieren. Röntgenstrukturanalysen von **4a** und **5a** bestätigen im wesentlichen die durch semiempirische Methoden erhaltenen Strukturvorschläge.

The transanular interaction between parallel C=C double bonds as in **1**, **2**, and **3** displays in different spectroscopical and photochemical properties of such compounds[2,3)]. Whereas the UV and PE spectra as well as the photoreactivity of norbornadiene (**1**) and barrelene (**2**) have been intensively studied, comparatively little information existed about the homoconjugative interaction between the C=C double bonds of the dechlorinated isodrin **3**.

The PE spectrum[4)] shows a particularly destabilized π orbital at 8.1 eV. A recent investigation of the photoreactivity[3)] of **3** shows its strong trend towards cyclization

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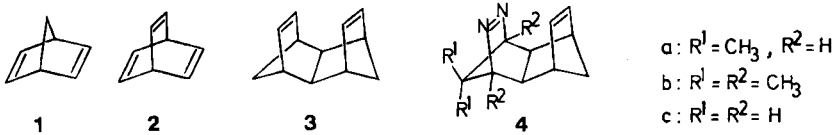
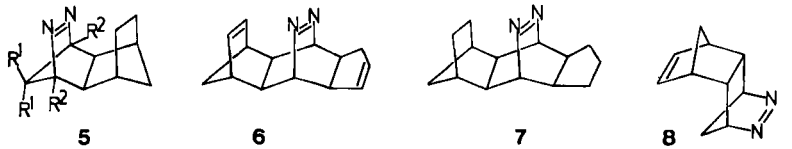
under direct as well as under sensitized photolysis ($\Phi \approx 0.5$ or 1.0). The UV spectrum of **3**[3] (intensive end absorption with a shoulder at 218 nm, $\varepsilon = 13000$ and $\varepsilon_{254} = 2000$) predicates little or nothing about the location of the long wavelength $\pi_- \rightarrow \pi_+^*$ transition which should be responsible for the photocyclization. This transition (symmetry forbidden in C_{2v}) might for two reasons be separately perceivable in diazaisodrins of type **4**[5]. On the one hand the reduced symmetry can remove or at least relax the forbiddenness of the transition, on the other hand the inductive effect of the N-atoms may cause a hypsochromic shift of possible perturbing $\sigma \rightarrow \pi^*$ excitations[6].

In the following the UV and PE spectra of **4** and its CC-hydrogenated derivatives **5** will be discussed.



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

a: $R^1 = CH_3$, $R^2 = H$
b: $R^1 = R^2 = CH_3$
c: $R^1 = R^2 = H$



5 **6** **7** **8**

a: $R^1 = CH_3$, $R^2 = H$
b: $R^1 = R^2 = CH_3$

Photoelectron and UV Spectra

Figure 1 shows the He(I)-PE spectra of **4a** and **5a**. The ionization energies are given in Table 1 and the UV excitation energies are given in Table 2.

Discussion of the PE Spectra

Empirical Correlations and ZDO Model

The first two PE bands of **3** can be related to the π_-^{-1} and π_+^{-1} ionization processes (see **9** and **10**)[4].

The replacement of a CC double bond by the N=N group should show the following predictable effects[7]:

a) stabilization of the π_- combination to a level with a dominating C=C contribution and

b) an energetically comparable ionization corresponding to the n_-^{-1} process,

c) an n_+ level which will be about 3 eV more stable than the n_- orbital,

d) a π_{NN} orbital which will be about 2.5 eV more difficult to ionize than the corresponding π_{CC} orbital.

1) The PE band at 8.60 eV in the spectrum of **4a** must contain the two ionization processes n_-^{-1} and π_{CC}^{-1}. The n_- ionizations of **5a** (8.40 eV) and **8** (8.80 eV) on the one hand and the fact that the π_{CC} orbital energy must be larger or the same as

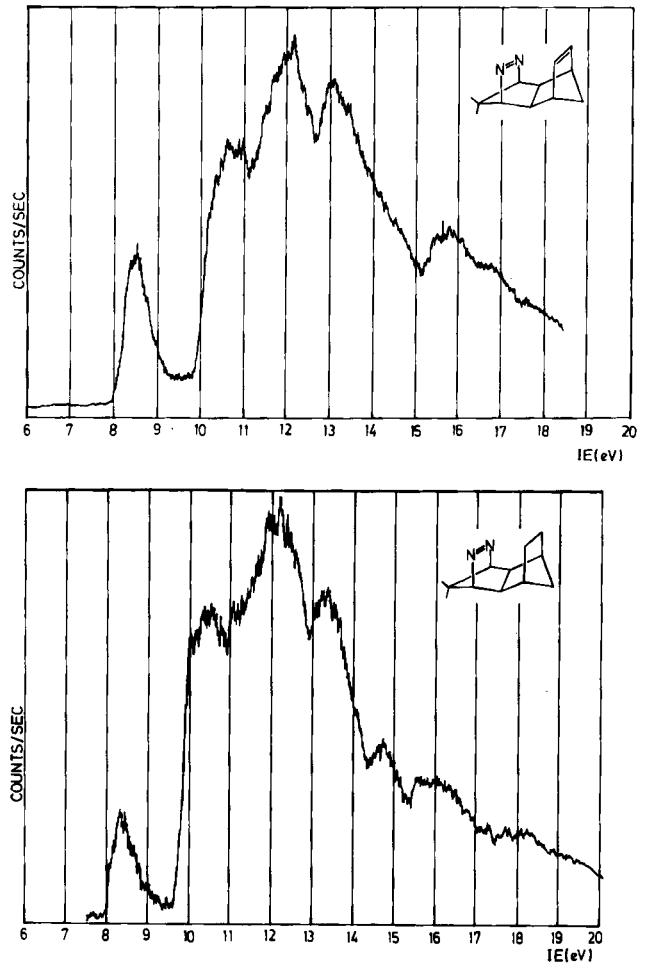


Figure 1. He(I)-PE spectra of **4a** and **5a**

Tab. 1. Vertical ionization energies of **3**[4], **4a**, **5a**, **6**[7a], **7**[7a], and **8**[7a] (in eV), values rounded to the nearest 0.1 or 0.05 eV

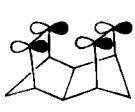
	$I_{m,1}$	$I_{m,2}$	$I_{m,3}$	$I_{m,4}$	$I_{m,5}$
3	8.10	9.35	10.00		
4a	8.60		10.45	to	11.10
5a	8.40		10.0	to	11.0
6	7.90	8.65	9.10	10.15	
7	7.95	9.90	to	11.0	
8	8.80	9.25	10.7	11.4	

in **8** (≥ -9.25 eV) on the other hand support this assumption. The probable homoconjugative interaction in **4a** can only have a destabilizing effect on the π_{CC} level.

2) The difference in n_- orbital energies that is observed in **4a** and **6**, respectively ($\Delta n_- = 0.7$ eV), corresponds exactly to the value found for the pair 2,3-diazabicyclo[2.2.2]oct-2-ene and 2,3-diazabicyclo[2.2.1]hept-2-ene ($\Delta n_- = 0.64$ eV[7b]). The lower n_- ionization energy of the [2.2.2]system roots a) in a geometrical difference as well as b) in a diverse degree of σ contribution. The NNC angle in **4a** is smaller than that of **6** by about 7°[7b,c]. The consequence will be a slight increase in the n_- ionization energy of **4a**. Since σ orbitals of suitable symmetry of mixing with n_- are higher in bicyclo[2.2.2]octane than in bicyclo-[2.2.1]heptane[7d], the destabilization of n_- in **6** is in part due to a more efficient contribution of the σ skeleton.

3) The location of the n_+ and π_{NN} levels can only be estimated. In **5a** the n_+ orbital should appear at about 8.40 + 2.95 = 11.35 eV and π_{NN} will supposedly be found at 8.40 + 2.5 = 10.9 eV[7a]. Therefore, the other bands which can be observed in this area must be ascribed to ionizations of the σ skeleton.

4) The empirical ZDO parameters of the homoconjugative interaction will naturally be affected with large inaccuracy since the unperturbed and perturbed π_{NN} levels are only accessible by estimations. The π_{CC} basis energy of **4a** is proved to be -8.9 eV (norbornene), but the π_{NN} basis energy of -10.9 eV (see 3)) is only estimated. An approximate effective interaction parameter of $H_{eff} \approx -0.8$ eV can be deduced. Despite the inaccuracy in $\varepsilon(\pi_{NN})$ this value is reasonable and corresponds with the parameters of other isodrins[7a] (**3**: -0.63 eV, **6**: -0.62 eV).



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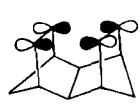

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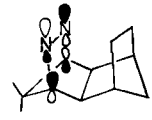

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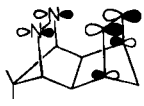

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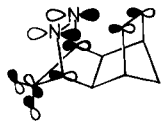

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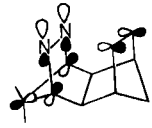

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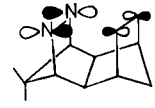

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MO Calculations

With the help of the MNDO method[8] the geometries of the diazaisodrins **4a** and **5a** were optimized. This method has proved reliable for the transanular distances in isodrins[7a,9]. The resulting geometries were therefore also used for other

methods, like: CNDO/2[10], HAM/3[11], STO-3G[12] and MINDO/3[13]. Table 3 shows the results of these calculations compared with the experimental ionization energies ($\varepsilon_i = -I_{m,i}$) of **4a**.

Tab. 2. UV Absorption, λ[nm] (ε), of **3**[3], **4a**, **4b**, **5a**, and **5b**[5]

3	(C_6H_{12})	218 (sh) (13000)	$\varepsilon_{254} = 2000$
4a	(C_6H_{14})	261 (236)	362 (386)
4b	(C_6H_{14})	260 (198)	369 (340)
5a	(C_6H_{14})		353 (612)
5b	(C_6H_{14})		359 (460)

Tab. 3. Comparison of orbital energies of **4a** with experimental values according to various methods (all values in eV), c(n_+): coefficient at N in the highest n_+ level

Orbital	CNDO/2	MNDO	HAM/3	STO-3G	MINDO/3	exp.
n_-	−11.81	−10.63	−7.90	−7.63	−8.42	−8.60
π_{CC}	−11.58	−9.63	−8.73	−7.33	−8.76	−8.60
π_{NN}	−14.26	−11.73	−10.64	−10.06	−9.97	−10.45 to −11.1
n_+	−13.71	−12.15	−10.84	−10.89	−9.48	
Δn	1.90	1.52	2.94	3.26	1.06	≈2.5
Δπ	2.68	2.10	1.91	2.73	1.21	≈2.5
c(n_+)	0.22	0.25	0.36	0.33	0.57	

Nearly all methods describe in particular the symmetrical combinations π_{NN} and n_+ as mostly delocalized molecular orbitals, that is to say there are several orbitals which are of n_+ character. This peculiarity has already been drawn attention to[7b]. The extent of the delocalization of the highest n_+ levels can be seen in the coefficients in Table 3. It would be wrong to say that there is only one single n_+ orbital. In **11** (n_-), **12** (π_{CC}), **13** (π_{NN}), and **14** (n_+) some molecular orbitals of **4a** with their most important atomic components are represented. Usually, bicyclic azo compounds show Δn values of about 3 eV[7a–c]. A comparison of these values with the results of the calculation methods in Table 3 shows, that HAM/3 and STO-3G are capable of reproducing this split far better than other methods and that especially MINDO/3 is dissatisfactory in that respect. The same applies to the Δπ split. However the absolute location of the two highest levels (n_- and π_{CC}) is very well predicted by MINDO/3. To get an idea of the extent of the influence of methyl groups MNDO calculations were performed for **4a, b**, and **c** which resulted in the optimized transanular distances of 289 pm for **4a** and **b** and 293 pm for **4c**. These values are in excellent correspondence to existing experimental data[7a]. An increasing number of methyl groups for the sequence **4c** < **4a** < **4b** effects an increasing destabilization of the levels n_-, π_{CC}, π_+^* and π_-^*.

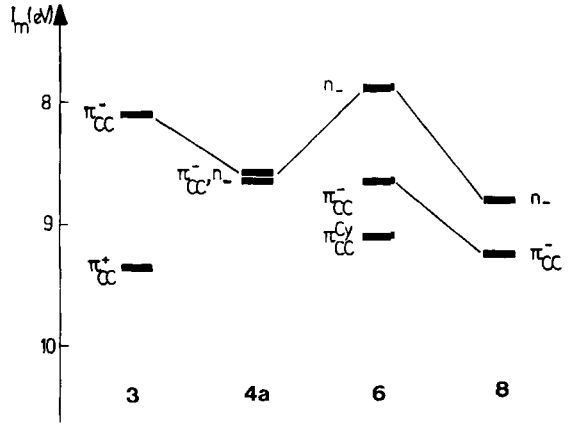


Figure 2. Correlation of the experimentally assigned n_- and π_{CC} ionization energies for **3**, **4a**, **6**, and **8**.
π_{CC}^-: Norbornene-type orbital, π_{CC}^{Cy}: Cyclopentene-type orbital

The average value for the effect of two methyl groups is 0.15 eV for n_-, 0.03 eV for π_{CC}, 0.04 eV for π_+^* and π_-^*. Figure 2 shows a correlation of the experimentally assigned levels n_- and π_{CC} for the abovementioned azo compounds.

Discussion of the UV Spectra

Empirical Assignment

In cyclic azo compounds the longest wavelenght singlet transition is of $n_- \rightarrow \pi^*$ type[14]. Therefore, the band at about 360 nm in **4** and **5**[5] must be related to this excitation. Methyl groups at the bridgehead atoms (**4a** → **4b**) cause a shift of 7 nm to higher wavelenghts. However, more interesting is the influence of the neighbouring CC double bonds. Hydrogenation (**4a** → **5a**) causes a hypsochromic shift of 9 nm to lower wavelenghts.

It is most unlikely that the second transition in **4** (at about 260 nm) is caused by another $n \rightarrow \pi^*$ excitation since this band does not appear in the spectra of hydrogenated derivatives. An obvious interpretation of this phenomenon would be to ascribe this band to the $\pi_- \rightarrow \pi_+^*$ transition which is symmetry forbidden in the norbornadiene (**1**)[15,16] and isodrin system **3**[3].

SCF-CI Calculations

CNDO-CI calculations[17] have proved reliable for calculating the $n_- \rightarrow \pi^*$ transition. Thus, the wavelenght of this excitation in 2,3-diazabicyclo[2.2.2]oct-2-ene (λ = 385 nm, log ε = 1.70) is very well predicted (experimental values: λ = 377 nm, log ε = 2.75)[7a]. Therefore, the excitation energies of **4** and **5** were calculated using the CNDO-S method[17] with forty singly excited configurations. Table 4 shows the results for **4a**, **4b**, **5a**, and **5b**.

There is excellent correspondence with the experimental absorption bands (see Table 2) and the transition at 260 nm (**4a** and **4b**) can be assigned to an almost

pure $\pi_- \rightarrow \pi_+^*$ configuration (**12** → **15**). The long-wave $n_- \rightarrow \pi_+^*$ transition, too, has been calculated as a dominating $n_- \rightarrow \pi_+^*$ excitation, i. e. **11** → **15**. The HAM/3 method also gives satisfying transition energies, but the influence of configuration interaction proves to be negligible. Concerning the influence of the methyl groups, it must be said, that the CNDO/S-CI as well as the HAM/3 method are inappropriate to reproduce the bathochromic shift of the $n_- \rightarrow \pi_+^*$ excitation. Neither is the hypsochromic shift, caused by hydrogenation of the CC double bond, reflected in the data of Table 4. Yet, the origin of both phenomena are obviously the following: an increasing number of methyl groups influences the σ-system and thus also the n_- level stronger than the π system. This is clearly proved by the abovementioned MNDO calculations. Since the $n_- \rightarrow \pi_+^*$ excitation is predominantly characterized by this configuration, the effect of the methyl groups can be attributed to a destabilization of the n_- orbital. In addition to that it is remarkable that the CNDO/S differences in orbital energies Δ (**4a**) = $\varepsilon(\pi_+^*) - \varepsilon(n_-)$ = 10.09 eV and Δ (**5a**) = $\varepsilon(\pi^*) - \varepsilon(n_-)$ = 10.14 eV, in contrast to the CI treat-

Tab. 4. Transition energies (eV), λ(nm), oscillator strengths, and state symmetries according to CNDO/S-CI for **4a**, **4b**, **5a**, and **5b**

	A′ ($n_- \rightarrow \pi_+^*$)	*f*	%	A″ ($\pi_- \rightarrow \pi_+^*$)	*f*	%
4a	3.36, 369	0.003	70.5	4.60, 270	0.000	95.7
	3.69, 336	0.002	–	4.19, 296	0.001	–
4b	3.37, 368	0.001	73.5	4.67, 266	0.000	97.3
	3.69, 336	0.002	–	4.29, 289	0.001	–
5a	3.33, 373	0.003	71.6	–	–	–
	3.69, 336	0.001	–	–	–	–
5b	3.38, 367	0.001	76.4	–	–	–
	3.69, 336	0.001	–	–	–	–

The first row for each compound gives the transition energies (eV), (state symmetry A′ or A″), λ(nm), and oscillator strengths according to CNDO/S-CI (40 configurations). The second row shows the results according to HAM/3 (without CI; inclusion of CI does not change the energies or intensities). The contribution of the designated configuration is given (%).

ment, give correct values for the hypsochromic shift of hydrogenated compounds and that the calculated difference of 0.05 eV corresponds to a shift from 362 nm to 356 nm, as it is observed. Thus, the longer wavelenght $n_- \rightarrow \pi_+^*$ absorption of **4a** compared to that of **5a** can be attributed to the lower lying π_+^* orbital of **4a** compared to the π^* orbital of **5a**. This transanular influence on the π^* energies has been proved experimentally in the isodrin **3** by electron transmission spectroscopy[18].

Structure Determination of 4a and 5a by X-ray Diffraction

As mentioned above the MNDO method is satisfactory for calculating the transanular distances in isodrins[7a]: **4a** 289 pm, **5a** 307 pm. The structure analyses

Tab. 5. Crystal data and summary of intensity data collection and structure refinement for **4a** and **5a**

Compound	**4a**	**5a**
crystal dimensions [mm]	0.35 × 0.7 × 0.25	0.15 × 0.35 × 0.1
number of measured intensities	1347	1011
number of observed reflections $F > 3\sigma(F)$	1206	887
number of structural factors whose phase relations lead to the structural determination	199	79
R_{aniso}	0.046	0.056
empirical formula	$C_{12}H_{16}N_2$	$C_{12}H_{18}N_2$
crystal class	monoclinic	monoclinic
space group (No.)	$P2_1/n$ (14)	$P2_1/m$ (11)
lattice constants	1024.9(9)	933.2(7)
a,b,c [pm]	1626.8(13)	940.1(8)
	613.9(5)	623.7(3)
β, deg (standard deviations)	92.81(7)	98.11(5)
molecules/unit cell	4	2
d calc. [g · cm^{-3}]	1.222	1.166

Tab. 6. Positional (× 10^4) and thermal (× 10^3) parameters (Å^2). U_{ij} is defined for $\exp[-2\pi^2(U_{11}b^2a^{*2} + \cdots 2U_{12}hka^*b^*)]$; numbers in parentheses represent standard deviations

4a

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C(1)	4128(2)	2309(1)	1038(4)	44(1)	50(1)	42(1)	2(1)	-4(1)	-3(1)
N(2)	2857(2)	2607(1)	1827(3)	66(2)	53(1)	46(1)	4(1)	16(1)	3(1)
N(3)	1990(2)	2478(1)	377(4)	44(1)	54(1)	67(1)	6(1)	18(1)	2(1)
C(4)	2613(2)	2087(2)	-1508(4)	38(1)	53(1)	53(1)	-8(1)	-2(1)	-2(1)
C(5)	3444(2)	2757(1)	-2555(3)	51(2)	53(1)	33(1)	-4(1)	1(1)	3(1)
C(6)	2976(3)	3649(2)	-3178(4)	55(2)	62(2)	46(1)	10(1)	-2(1)	7(1)
C(7)	2369(3)	4061(2)	-1270(4)	61(2)	49(1)	70(2)	10(1)	15(2)	15(1)
C(8)	3305(3)	4194(1)	236(4)	89(2)	39(1)	60(2)	-5(1)	14(2)	5(1)
C(9)	4566(3)	3873(1)	-602(4)	60(2)	45(1)	63(2)	3(1)	-6(1)	-8(1)
C(10)	4527(2)	2909(1)	-782(4)	33(1)	48(1)	49(1)	2(1)	2(1)	-1(1)
C(11)	4320(3)	4064(2)	-3032(4)	66(2)	60(2)	67(2)	17(1)	15(1)	2(2)
C(12)	3659(2)	1553(1)	-312(4)	39(1)	43(1)	57(1)	-0(1)	3(1)	-1(1)
C(13)	3102(3)	870(2)	1102(5)	58(2)	52(1)	94(2)	14(2)	6(2)	-4(1)
C(14)	4653(3)	1158(2)	-1766(5)	59(2)	55(2)	88(2)	-12(2)	11(2)	8(1)

5a

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C(1)	9418(2)	1327(3)	2824(3)	55(1)	47(1)	47(1)	5(1)	9(1)	6(1)
N(2)	8909(2)	1828(2)	4878(3)	51(1)	72(1)	42(1)	8(1)	3(1)	3(1)
C(3)	8206(2)	1668(2)	920(3)	52(1)	51(1)	44(1)	-7(1)	4(1)	-3(1)
C(4)	6576(3)	1292(3)	838(4)	52(1)	68(2)	68(2)	-13(1)	5(1)	-12(1)
C(5)	5938(3)	1671(3)	2904(4)	50(1)	74(2)	72(2)	2(1)	14(1)	-10(1)
C(6)	5945(4)	2500	-688(6)	49(2)	126(4)	58(2)	0	-7(2)	0
C(7)	557(3)	2500	2551(5)	46(2)	56(2)	43(2)	0	3(1)	0
C(8)	1853(4)	2500	4379(6)	45(2)	124(4)	57(2)	0	2(2)	0
C(9)	1159(4)	2500	386(5)	53(2)	72(2)	54(2)	0	17(2)	0

Tab. 7. Bond lengths in pm and angles in deg (standard deviations)

4a

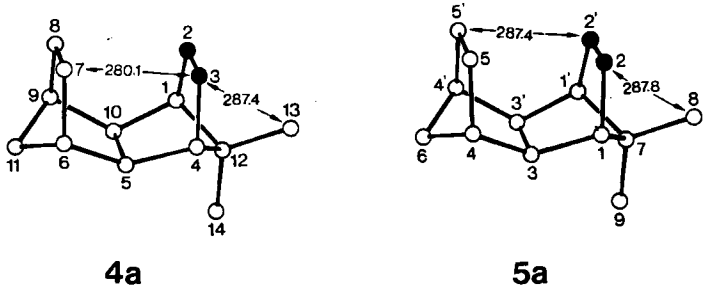
C(1)	– N(2)	149.3(3)	N(2)	– C(1)	– C(10)	107.1(2)
C(1)	– C(10)	155.3(3)	N(2)	– C(1)	– C(12)	100.3(2)
C(1)	– C(12)	154.7(3)	C(10)	– C(1)	– C(12)	101.6(2)
N(2)	– N(3)	124.5(3)	C(1)	– N(2)	– N(3)	108.5(2)
N(3)	– C(4)	149.2(3)	N(2)	– N(3)	– C(4)	108.0(2)
C(4)	– C(5)	154.3(3)	N(3)	– C(4)	– C(5)	106.7(2)
C(4)	– C(12)	153.9(3)	N(3)	– C(4)	– C(12)	100.7(2)
C(5)	– C(6)	157.0(3)	C(5)	– C(4)	– C(12)	102.2(2)
C(5)	– C(10)	153.6(3)	C(4)	– C(5)	– C(6)	125.9(2)
C(6)	– C(7)	151.0(4)	C(4)	– C(5)	– C(10)	102.3(2)
C(6)	– C(11)	153.3(4)	C(6)	– C(5)	– C(10)	103.1(2)
C(7)	– C(8)	131.7(4)	C(5)	– C(6)	– C(7)	110.7(2)
C(8)	– C(9)	150.7(4)	C(5)	– C(6)	– C(11)	97.4(2)
C(9)	– C(10)	157.3(3)	C(7)	– C(6)	– C(11)	99.3(2)
C(9)	– C(11)	153.3(4)	C(6)	– C(7)	– C(8)	107.7(2)
C(12)	– C(13)	153.7(4)	C(7)	– C(8)	– C(9)	108.1(2)
C(12)	– C(14)	152.8(4)	C(8)	– C(9)	– C(10)	110.5(2)
			C(8)	– C(9)	– C(11)	99.2(2)
			C(10)	– C(9)	– C(11)	97.6(2)
			C(1)	– C(10)	– C(5)	101.6(2)
			C(1)	– C(10)	– C(9)	125.6(2)
			C(5)	– C(10)	– C(9)	103.0(2)
			C(6)	– C(11)	– C(9)	94.1(2)
			C(1)	– C(12)	– C(4)	89.8(2)
			C(1)	– C(12)	– C(13)	112.8(2)
			C(1)	– C(12)	– C(14)	116.7(2)
			C(4)	– C(12)	– C(13)	114.1(2)
			C(4)	– C(12)	– C(14)	115.3(2)
			C(13)	– C(12)	– C(14)	107.7(2)

5a

C(1)	– N(2)	150.3(3)	N(2)	– C(1)	– C(3)	107.3(2)
C(1)	– C(3)	155.3(3)	N(2)	– C(1)	– C(7)	100.0(2)
C(1)	– C(7)	155.8(3)	C(3)	– C(1)	– C(7)	101.8(2)
N(2)	– N(2')	126.3(4)	C(1)	– N(2)	– N(2')	108.3(1)
C(3)	– C(3')	156.5(4)	C(1)	– C(3)	– C(3')	101.9(1)
C(3)	– C(4)	155.5(3)	C(1)	– C(3)	– C(4)	125.6(2)
C(4)	– C(5)	153.6(4)	C(4)	– C(3)	– C(3')	103.1(1)
C(4)	– C(6)	154.4(3)	C(3)	– C(4)	– C(5)	114.4(2)
C(5)	– C(5')	155.9(5)	C(3)	– C(4)	– C(6)	98.0(2)
C(7)	– C(8)	154.0(4)	C(5)	– C(4)	– C(6)	100.8(2)
C(7)	– C(9)	153.4(5)	C(4)	– C(5)	– C(5')	103.4(1)
			C(4)	– C(6)	– C(4')	94.7(3)
			C(1)	– C(7)	– C(1')	90.1(2)
			C(1)	– C(7)	– C(8)	113.3(2)
			C(1)	– C(7)	– C(9)	115.9(2)
			C(8)	– C(7)	– C(9)	107.7(3)

verify the absolute distance as well as the increased distance caused by hydrogenation: **4a** 280 pm, **5a** 287 pm. The measured transanular distances of 287 pm and 282 pm between the two N=N double bonds in an asymmetric tetraaza derivative also lie in this range[19].

Colourless, transparent crystals of **4a** and **5a** could be obtained from *n*-hexane. Their cell parameters were determined basing on 15 reflections on a Syntex-P3-four-circle diffractometer. Measurement of the intensities: ω-scan, Mo-K_α, scan range = 1°, $2\theta_{max.}$ = 55°. Evaluation with the programme SHELXTL 83 on an Eclipse S/250. The signs of the number of structural factors listed in Table 5 and thus the atomic positions of the molecules could be determined by direct methods. The refinements of the parameters by anisotropic least-squares cycles lead to the given *R* values. The positions of the hydrogen atoms were calculated geometrically and considered isotropically in all refinements[20].



4a **5a**

Figure 3. Perspective drawing of the molecules with the labeling of the atoms corresponding to Tables 6 and 7

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