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The Molecular and Crystal Structures of Two Diastereomeric 3,4-Dihydropyrromethenones**

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The molecular and crystal structures of the two racemic diastereomeric 3,4-dihydropyrromethenone derivatives **1** and **2** of configurations (*Z*) and (*E*) were determined at 93 K (**1**, **2**) and at room temperature (**1**). From an analysis of the crystallographically observed temperature coefficients a pseudorotation flexibility of the pyrrolidinone ring in the crystal is deduced. In both compounds a nearly orthogonal arrangement between the two heterocyclic ring systems is observed, which is ascribed to the steric bulk of the substituents in positions 1 and 3 of the pyrrolidinone ring.

(Keywords: 3,4-Dihydropyrromethenone; Molecular conformation of 3,4-dihydropyrromethenones; Phytochrome model compounds; Temperature factor analysis)

Die Struktur zweier diastereomerer 3,4-Dihydropyrromethenone

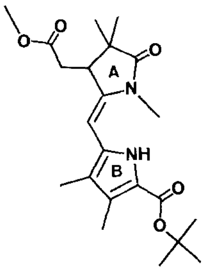
Die Molekül- und Kristallstruktur der beiden racemischen diastereomeren 3,4-Dihydropyrromethenonderivate **1** und **2** mit Konfigurationen (*Z*) und (*E*) wurden bei 93 K (**1**, **2**) und bei Raumtemperatur (**1**) bestimmt. Aus einer Analyse der kristallographisch beobachteten Temperaturfaktoren wird auf eine Pseudorotations-Flexibilität des Pyrrolidinonringes im Kristall geschlossen. In beiden Verbindungen beobachtet man eine nahezu orthogonale Orientierung der beiden Fünfringe zueinander, die der Raumerfüllung der Substituenten in Positionen 1 und 3 des Pyrrolidinonringes zugeschrieben wird.

Introduction

Investigation of chemical, spectroscopic and structural properties of partial structures is used extensively in the study of linear tetrapyrroles.

** Herrn Prof. *Josef Schurz* zum 60. Geburtstag gewidmet.

The biochemical significance of this class of compounds with its immense constitutional, conformational and tautomeric variability has attracted increasing attention, particularly since it became evident that the photoreceptor molecule of the plant pigment phytochrome is also a linear tetrapyrrole of the 2,3-dihydrobilatriene type. Phytochrome is responsible for the photomorphogenesis. Several forms of phytochrome are spectroscopically discernible, which are interconverted by light and/or thermal dark reactions. It is highly probable that at least some of these spectroscopic forms are associated with different constitutions, diastereomers or conformations of the phytochromobilin molecule[1].



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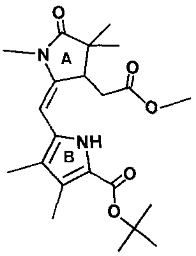

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In the present communication, we report the crystal structures of the two diastereomeric 3,4-dihydropyrromethenones **1** and **2**, both in racemic form. The two molecules differ only with respect to the configuration about the exocyclic double bond, leading to (*Z*) and (*E*) forms (**1** and **2**). Formally, the chromophore of **1** is identical to the "left half" of the chromophore of the phytochromobilin molecule, for which (*Z*)/(*E*) diastereomerism is occasionally discussed as being involved in its biological function. Both compounds were prepared in the course of an extensive series of investigations of differently substituted dihydropyrromethenones[2], which demonstrated—among other—that the relative thermodynamic stabilities of (*Z*) versus (*E*) forms in dihydropyrromethenones depends on the relative bulk of the substituents in position 3 and on the lactam nitrogen atom. Thus, while the (*Z*)-configuration is thermodynamically favoured for compounds with a proton on the lactam nitrogen, methylation at this position—as in compounds **1** and **2**—inverts the thermodynamic stabilities and makes the (*E*)-diastereomer more stable.

The crystal structures were determined to contribute to the understanding of the above situation. Also, the conformation about the formal exocyclic single bond was of interest: the large substituents on the pyrrolidine ring made a highly non-coplanar conformation of the two heterocyclic rings probable, and it was of interest to observe the effect of a large twist angle on the length of the (formal) exocyclic single bond.

To our knowledge, only three crystal structures of dihydropyrromethenones have appeared in the literature so far[3]; they are the structures of the (*Z*) and (*E*) isomers of 5′-ethoxycarbonyl-3,4-dihydro-3′,4′-dimethyl-5(1*H*)-2,2′-pyrromethenone and the (*E*)-isomer of the same compound with an ethyl group in place of the lactam proton. We will use the results of these structure determinations in the subsequent discussion of our structures. Another structural investigation of a (*Z*)-derivate was announced in a preliminary communication[4].

Both structure determinations reported in this communication were carried out at low temperature (93 K) to attain maximum accuracy. The structure of **1** was also determined at room temperature; the combination of room temperature and low temperature data permits a test on the presence or absence of static disorder in the crystal. Finally, we will present the results of an analysis of the temperature factors for the two low temperature structures to obtain an indication about the flexibility of the molecules in the crystal.

Results and Discussion

Tables 1 and 2 list atomic coordinates and equivalent isotropic temperature coefficients with associated standard deviations for the room temperature structure of **1** and for the two low-temperature structures, for which anisotropic temperature coefficients are given in Table 3. Bond lengths and bond angles calculated from the low-temperature coordinates are summarized in Fig. 1, which also defines the atom numbering used.

Molecular Constitution and Conformation

The structure analyses (Figs. 2 and 3) confirm the (*Z*)- and (*E*)-configurations for **1** and **2**, respectively. As expected, both structures display pronounced non-planarity between the two five membered rings; the large values observed for the twist angle about the $C_\alpha - C_m$ single bond (C4-C5-C6-N11, Fig. 1) make a classification of the conformation in terms of "*syn*" or "*anti*" somewhat pointless; however, since both torsion angles have absolute values beyond 90°, the two molecules should most appropriately be termed (*Z*)- and (*E*)-anticlinal, respectively.

The main factor responsible for the anticlinal conformation is probably steric repulsion between the substituents on the pyrrole and the pyrrolidine rings, which prohibits a periplanar conformation. The exact value of the C5 – C6 dihedral angle, however, may well be significantly

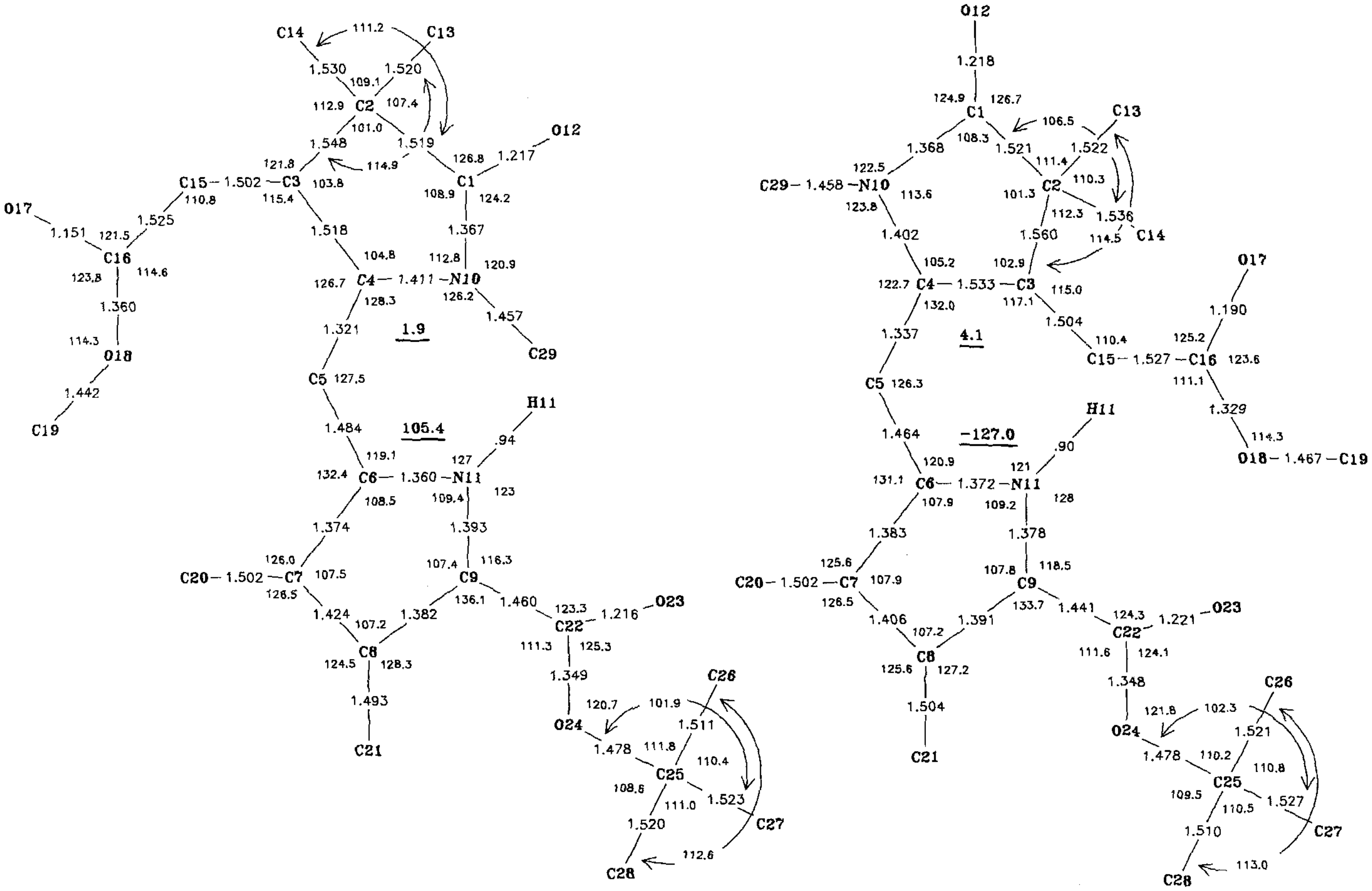

Fig. 1. Calculated bond lengths and bond angles for the low temperature crystal structures of **1** (left) and **2** (right). Two torsion angles about the two C_m-C_α-bonds are also given (underlined). Derived standard deviations are as follows: **1**: $X-Y$, $\sigma\sim.005-.001$; N−H, $\sigma\sim.05$ Å; $X-Y-Z$, $\sigma\sim0.4-0.6$; $X-$N−H, $\sigma\sim2.8°$; **2**: $X-Y$, $\sigma\sim.003-.005$; N−H, $\sigma\sim.03$ Å; $X-Y-Z$, $\sigma\sim0.2-0.3°$; $X-$N−H, $\sigma\sim2.0°$ (X, Y, Z = C, N, O)

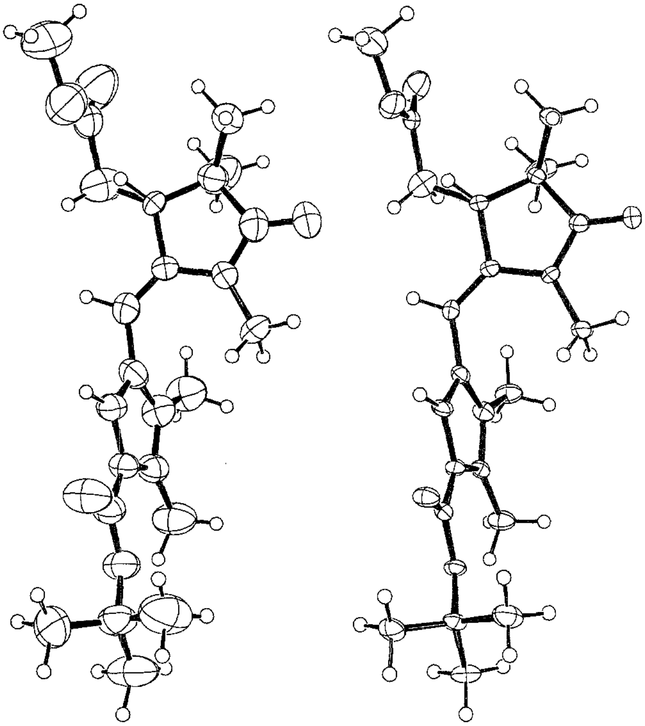

Fig. 2. ORTEP drawing of the room temperature (left) and low temperature crystal structures (right) of **1**. Temperature ellipsoids of C, N and O are drawn at the 50% level; H atoms are represented as spheres of radius 0.1 Å

influenced by intermolecular hydrogen bonding (see below) and dispersion forces, whose collective effect is difficult to assess.

The degree of conjugation across the formal C_m-C_α "single" bond is frequently discussed in crystal structures of linear di- and tetrapyrroles. Fig. 4 shows a plot of the C 5 – C 6 bondlength versus the absolute value of the dihedral angle about this bond for the three structure determinations on **1** and **2** and for the three dihydropyrromethonone crystal structures described in Ref.[3]. In spite of the limited data, there clearly is a positive correlation between dihedral angle and bond length, which varies between 1.44 and 1.50 Å for $\tau = 0$ and 90°, respectively. It is well established that the conjugation across the "single" bond is more pronounced in pyrromethenones[5], whose corresponding bond length is observed at about 1.43 Å for the periplanar conformation.

As observed in previously reported dihydropyromethenone structures[3], the ester carbonyl group is approximately coplanar with the

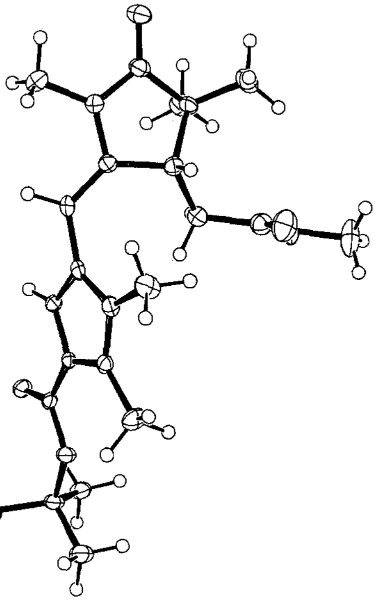

Fig. 3. ORTEP drawing of **2** as observed in its low temperature crystal structure

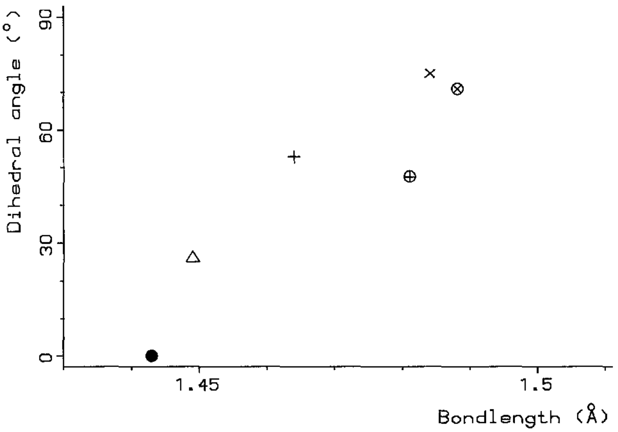

Fig. 4. Plot of the $C_5 - C_6$ bond length versus the absolute value of the smaller of the two torsion angles for 6 crystal structure determinations of dihydropyrromethenones. × **1**, low temperature; ⊗ **1**, room temperature, + **2**, low temperature; ⊕ compound I, ● compound II, Δcompound IV from Ref.[3]

pyrrole ring (torsion angles C 8 – C 9 – C 22 – O 24: – 8.5° in **1** and 4.4° in **2**), with the carbonyl oxygen syn to the pyrrole nitrogen.

The lower free enthalpy of **2** as opposed to **1** has been ascribed to the effect of steric repulsion between the methyl group on the lactam nitrogen and the pyrrole ring[2]. Indeed, there is crystallographic evidence in support of this explanation: both, the C 29 – N 10 – C 4 and N 10 – C 4 – C 5 angles are significantly larger in **1** than in **2** (by 2.4° and 5.6°, respectively); these are the largest differences between corresponding angles in the two structures.

Pyrrolidine Ring Conformation

While the pyrrole ring is planar within experimental error in both compounds, the pyrrolidine rings show significant deviations from planarity. The conformation of five-membered rings is conveniently described in terms of a puckering amplitude q and a phase angle $\emptyset$, using the equation for a pseudorotating pentagon[6]

$$Z_j = (2/5)^{1/2} \cdot q \cdot \cos(4\pi j/5 + \emptyset)$$

(Z_j is the normal deviation of atom j from a least-squares plane through the five-membered ring). The values observed in the two structures are $q = 0.291$ (**1**) and 0.294 Å (**2**) and $\emptyset$ (mod 36) = 28.2 (**1**) and 23.3° (**2**), respectively.

Since $\emptyset$ (mod 36) – values of 0° or 36° correspond to envelope and of 18° to twist conformations, the pyrrolidine rings are intermediate between envelope and twist forms in both structures.

The puckering amplitudes are remarkably large in both compounds, compared to values between 0.06 and 0.11 Å observed in other dihydropyrromethenone crystal structures[5]. We searched the Cambridge Crystallographic Data File[7] for pyrrolidine rings with exocyclic double bonds in positions 2 and 5 and obtained 18 structures containing such a fragment. The average value of q for those 18 rings was 0.093 Å, the largest value was 0.23 Å. We ascribe the large value of q in **1** and **2** to the effect of the large substituents on C 2 and C 3, which appear to enforce a more or less staggered conformation between the methyl groups on C 2 and the acetic acid ester group on C 3 (torsion angles C 13 – C 2 – C 3 – C 15: – 45.1° in **1** and – 83.2° in **2**; C 14 – C 2 – C 3 – C 15: 80.9° in **1** and 43.6° in **2**.

Packing

Both compounds have an "acidic" hydrogen (H 11 on the pyrrole nitrogen atom N 1) capable of forming an intermolecular H-bond to any of the carbonyl oxygen atoms. As expected, this H-bond has a decisive influence on the packing of both structures (Fig. 6).

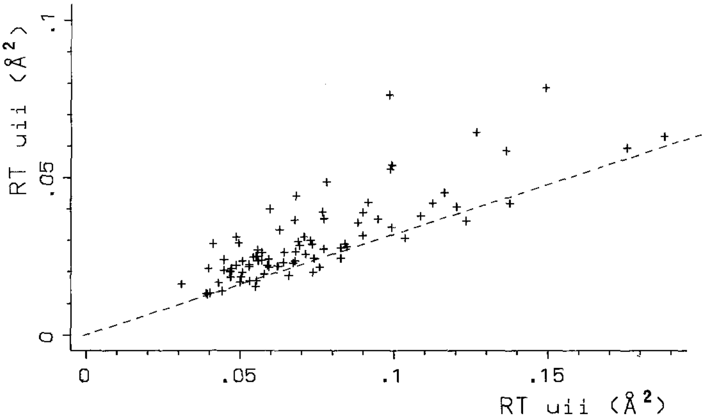

Fig. 5. Scatterplot of room temperature u_{ii} values (abscissa) versus the corresponding low temperature values for the crystal structure of **1**

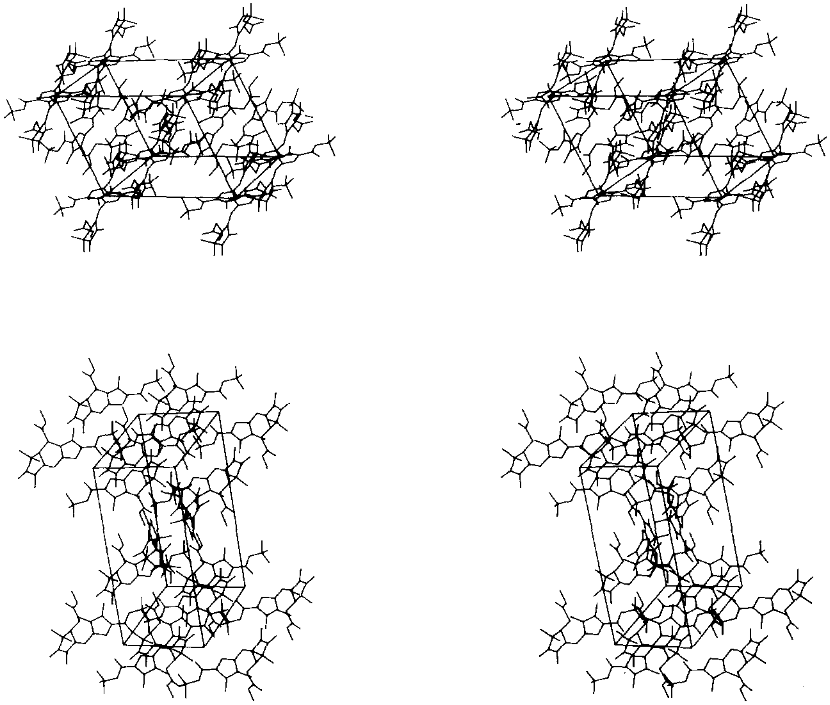

Fig. 6. Stereoscopic packing diagrams for the crystal structures of **1** (top) and **2** (bottom). The crystallographic axes are oriented as follows: **1**: *X* towards the viewer, *Y* left to right, *Z* upwards **2**: *X* upwards, *Y* towards the viewer, *Z* left to right

In **1** the H-bond involves the lactam oxygen atom of ring A (H 11 $-$O $12_{-1/2-x,-1/2+y,-z}$, $d = 1.95$ Å) of a molecule related by the operation of the 2_1 screw axis, leading to the formation of one-dimensional chains of molecules running along the monoclinic axis. The packing of **2**, on the other hand, is dominated by the formation of centrosymmetric dimers involving the carbonyl oxygen of the *t*-butylester grouping (H 11 $-$O $23_{-x,-y,2-z}$, $d = 1.99$ Å).

No pronounced base-stacking is observed in either one of the two structures.

Comparison of Room Temperature and Low Temperature Structures of **1**

Fig. 2 shows ORTEP-drawings of the asymmetric unit of **1** as observed at the two temperatures; a scatterplot of low-temperature (LT) versus room-temperature (RT) u_{ii} values for the anisotropically refined atoms (i.e. C, N, O) is shown in Fig. 5. To a first approximation (each atom vibrating independently in a harmonic potential[6,8,9]), such a plot should yield a straight line through the origin with slope T_1/T_2 (T is the absolute temperature). This line (with slope $93/293 \approx 0.32$) is also indicated in the plot, and it is evident that the LT u_{ii} values are systematically higher than predicted by the model. Barring experimental errors, the discrepancy is most probably due to inherent limitations of the harmonic approximation, in particular the effect of zero-point vibrations. Nevertheless, the plot gives little indication for disorder in the structure.

As expected, RT bond lengths are systematically shorter [by 0.005 (1) Å] than LT ones. The difference is readily explained as the result of anisotropic libration.

Analysis of Vibration Ellipsoids

Energies involved in bond stretching are large compared to those associated with other deformations in a crystal (lattice vibrations, torsion and bond angle deformations). Therefore, mean square vibrational amplitudes of atoms connected by a chemical bond should be approximately equal along the bond direction[11]. This property, which should also hold for any two atoms belonging to a rigid group, can be used to test the applicability of the rigid-body model to a molecule or molecular group[12]: with Z_{kl}^2 being the mean-square vibration amplitude of atom k along the line connecting atoms k and l, the test calls for computation of the $n \times n$ matrix of $\Delta_{kl} = Z_{kl}^2 - Z_{lk}^2$ values (n = number of atoms), and accepts the rigid-body assumption if all the Δ-values are zero within experimental error.

Δ-values differing significantly from zero indicate non-rigidity. U_{ij} values from structure refinement against X-ray data are prone to systematic errors and tend to absorb charge-density deformation contributions. However, the fact that Δ-values along chemical bonds should always be zero (see above) can serve as an indication for the usability of the u_{ij} values at hand.

Instead of Δ_{kl}, we will in the following use $\delta_{kl} = \Delta_{kl}/\sigma(\Delta_{kl})$, thereby replacing differences in mean square vibrational amplitudes by their statistical significance.

In the course of an analysis of the temperature factors for molecular flexibility, two types of question may be encountered: (1) does a fragment behave as a rigid group and (2) does one rigid fragment "vibrate" relative to a second rigid fragment? Within the inherent limits of this approach, both types of questions can be treated by inspection of the appropriate elements of the δ matrix. To check whether all elements of the corresponding subset of the δ_{kl} matrix are zero within experimental error, we use the well-known technique of the half normal probability plot (HNPP)[9], which amounts to a plot of the δ_{kl} versus their statistical expectation values. If the hypothesis of zero δ_{kl} is fulfilled, the plot yields a straight line through the origin with unit slope. A HNPP with slope < 1 indicates δ_{kl} systematically different from zero or underestimation of the $\sigma(\Delta_{kl})$.

In the present application, Δ_{kl} were computed from the U_{ij} derived from the least squares refinement. Their associated standard deviations $\sigma(\Delta_{kl})$ were obtained from the $\sigma(U_{ij})$, neglecting covariant terms.

Flexibility of **1** *and* **2** *in the Crystal*

A first rough indication of the most flexible regions can be obtained from the equivalent isotropic temperature factors listed in Table 1: in all three structures, the largest u_{iso} values are found for the atoms of the methyl ester and for the ring A substituents, while the atoms of ring B and the *t*-butylester show u_{iso} values below average.

The HNPP of δ_{kl} along chemical bonds is shown in Fig. 7 A for the low-temperature data of **1**. Since δ_{kl} along bond directions should be zero, the figure is no more than a test for the quality of the data. Evidently, the plot shows a slope less than unity (~ 0.62), which will have to be born in mind for the interpretation of the following HNPP's.

Fig. 7 B shows a HNPP of the δ_{kl} for all intra-fragment vectors involving the pyrrole ring atoms and the atoms directly attached to it. Since δ_{kl} values are insensitive to out-of-plane vibrations of planar groups[9], the observed slope of ~ 0.95 is as expected and yields another test for the quality of the u_{ij} values.

The analogous HNPP for the pyrrolidine ring (Fig. 7 C) is strikingly different: with an observed slope less than 0.3, we can safely conclude that

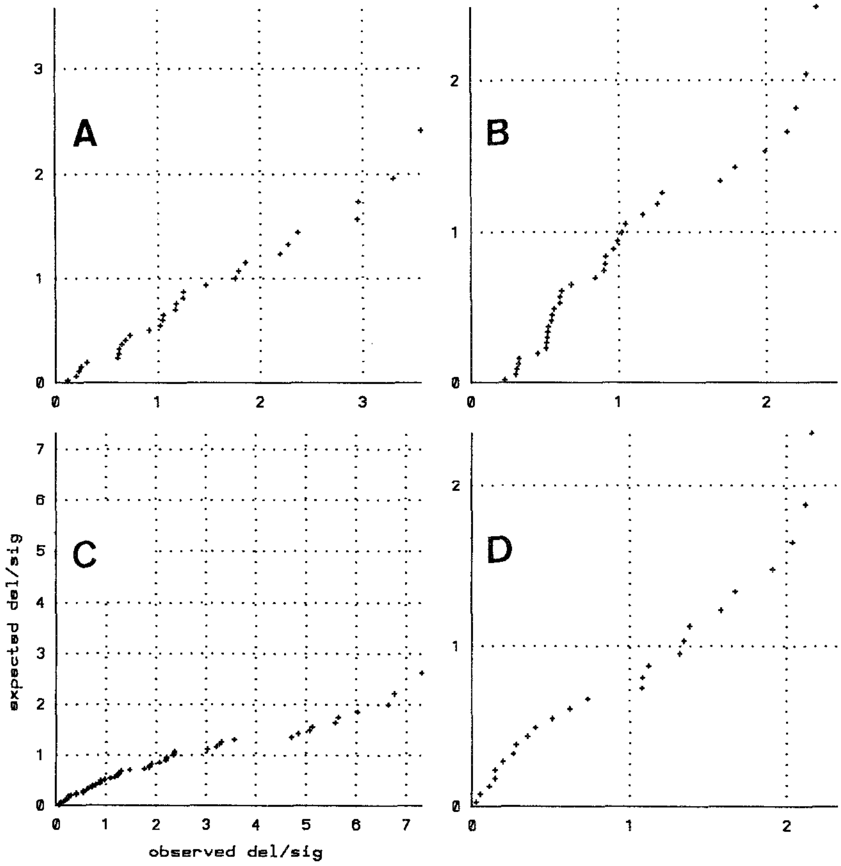

Fig. 7. Half-normal probability plots of δ_{kl} from the low-temperature structure of **1** (see text): A: k, l = all pairs of bondes atoms; *B*: k, l = atoms 1–5, 10, 12–15, 29; C: k, l = 5–9, 11, 20–22; D: k = 6, 9, 11, 28, 29; l = 1, 2, 3, 4, 10

the ring shows "flexibility" in the crystal, i.e. the observed u_{ij} are not compatible with a rigidly librating molecular fragment. Non-planar five-membered rings are known to show pseudorotation, which makes the above result quite plausible.

A more unexpected result emerges from Fig. 9 D, which shows a HNPP of the δ_{kl} for vectors between pyrrole and pyrrolidine ring. Since these two fragments are connected by a formal single bond, one might anticipate that they librate more or less independently. However, the HNPP yields no experimental evidence to reject a rigid-molecule

Table 1. *Atomic coordinates and equivalent isotropic temperature factors* ($\cdot 10^4$, *U-values in* $\mathring{A}^2$) *for the non-hydrogen atoms in the crystal structures of* **1** (*A: room temperature, B: low temperature*) *and* **2** (*C: low temperature*). Estimated standard deviations are given in italics. The equivalent isotropic temperature factors were obtained as one third of the trace of the orthogonalized U_{ij} tensor, and it corresponds to an isotropic temperature factor of the form $T = \exp(-8\pi^2 \cdot u \cdot \sin^2 \vartheta/\lambda^2)$

	A								B								C							
Atom	X/a		Y/b		Z/c		Ui so		X/a		Y/b		Z/c		Ui so		X/a		Y/b		Z/c		Ui so	
C1	−3060	*7*	3549	*6*	−1006	*5*	628	*60*	−3098	*4*	3545	*4*	−995	*3*	243	*31*	−4271	*3*	5186	*3*	8808	*2*	245	*17*
C2	−3188	*6*	2884	*6*	−1814	*4*	538	*54*	−3223	*4*	2876	*4*	−1824	*3*	267	*32*	−4117	*2*	4497	*3*	8130	*2*	224	*16*
C3	−2572	*7*	1815	*6*	−1395	*4*	776	*60*	−2584	*5*	1790	*6*	−1407	*4*	458	*41*	−2781	*2*	4387	*3*	8232	*1*	209	*16*
C4	−1713	*7*	2172	*6*	−517	*4*	478	*53*	−1687	*4*	2157	*4*	−521	*3*	251	*31*	−2424	*2*	4297	*3*	9027	*1*	181	*15*
C5	−770	*7*	1649	*6*	−25	*5*	600	*60*	−702	*5*	1634	*5*	−47	*3*	255	*32*	−1485	*3*	3795	*3*	9433	*1*	199	*16*
C6	69	*6*	1916	*6*	876	*5*	537	*57*	115	*4*	1911	*4*	862	*3*	212	*29*	−468	*2*	3241	*3*	9198	*1*	184	*15*
C7	905	*7*	2731	*6*	1190	*5*	560	*57*	950	*4*	2730	*4*	1182	*3*	228	*30*	255	*2*	3813	*3*	8791	*1*	202	*15*
C8	1429	*6*	2583	*6*	2120	*4*	514	*55*	1488	*4*	2576	*4*	2118	*3*	185	*28*	1122	*2*	2853	*3*	8739	*1*	189	*15*
C9	898	*6*	1685	*6*	2334	*4*	452	*53*	943	*4*	1672	*4*	2340	*3*	203	*28*	918	*2*	1707	*3*	9126	*1*	160	*15*
N10	−2190	*5*	3131	*5*	−309	*3*	558	*45*	−2187	*3*	3117	*3*	−294	*3*	229	*25*	−3308	*2*	4946	*3*	9296	*1*	218	*14*
N11	75	*5*	1286	*5*	1570	*4*	522	*45*	106	*3*	1271	*4*	1556	*3*	219	*26*	−55	*2*	1961	*3*	9402	*1*	178	*13*
O12	−3624	*4*	4370	*4*	−974	*3*	762	*37*	−3672	*3*	4358	*3*	−950	*2*	280	*21*	−5116	*2*	5808	*2*	8915	*1*	365	*14*
C13	−2532	*11*	3517	*7*	−2309	*6*	933	*82*	−2622	*5*	3529	*7*	−2357	*4*	454	*44*	−4663	*3*	5337	*4*	7499	*2*	347	*20*
C14	−4511	*7*	2740	*7*	−2392	*6*	853	*62*	−4531	*5*	2701	*5*	−2393	*4*	355	*35*	−4697	*3*	3084	*4*	8120	*2*	320	*20*
C15	−2119	*10*	1030	*9*	−1869	*6*	1122	*82*	−2123	*7*	992	*7*	−1927	*5*	592	*51*	−2339	*3*	3287	*3*	7807	*2*	244	*17*
C16	−3098	*9*	566	*7*	−2668	*6*	809	*77*	−3136	*5*	546	*5*	−2728	*4*	399	*38*	−2435	*3*	3749	*4*	7050	*2*	283	*18*
O17	−3208	*7*	641	*5*	−3380	*4*	1262	*64*	−3264	*4*	829	*3*	−3440	*3*	505	*31*	−2119	*2*	4827	*3*	6866	*1*	406	*15*
O18	−3792	*7*	−200	*5*	−2521	*4*	1046	*55*	−3810	*4*	−247	*3*	−2533	*2*	476	*29*	−2884	*2*	2765	*2*	6612	*1*	351	*14*
C19	−4603	*11*	−732	*11*	−3317	*8*	1325	*91*	−4634	*6*	−793	*6*	−3301	*5*	466	*44*	−2992	*4*	3129	*5*	5873	*2*	484	*28*
C20	1163	*7*	3611	*7*	647	*5*	791	*73*	1217	*5*	3641	*5*	644	*3*	321	*35*	118	*3*	5209	*4*	8458	*2*	310	*20*
C21	2363	*7*	3287	*7*	2700	*5*	826	*70*	2441	*5*	3300	*5*	2719	*4*	315	*34*	2085	*3*	3050	*4*	8338	*2*	293	*19*
C22	930	*7*	1166	*7*	3148	*5*	534	*59*	972	*4*	1136	*4*	3161	*3*	217	*30*	1477	*2*	395	*3*	9259	*1*	182	*15*
O23	277	*5*	462	*5*	3187	*3*	810	*45*	268	*3*	427	*3*	3188	*2*	277	*23*	1125	*2*	−534	*2*	9586	*1*	232	*12*
O24	1775	*4*	1612	*4*	3847	*3*	618	*38*	1838	*3*	1563	*3*	3874	*2*	216	*20*	2435	*2*	317	*2*	8977	*1*	204	*11*
C25	1885	*8*	1323	*7*	4766	*4*	664	*67*	1929	*4*	1255	*4*	4786	*3*	228	*31*	3130	*2*	−951	*3*	9015	*2*	218	*16*
C26	2096	*10*	119	*8*	4913	*6*	911	*84*	2067	*5*	20	*5*	4935	*4*	324	*38*	3620	*3*	−1294	*4*	9771	*2*	268	*18*
C27	2987	*9*	1963	*11*	5304	*5*	985	*94*	3060	*5*	1853	*6*	5347	*4*	324	*37*	4085	*3*	−544	*4*	8621	*2*	291	*19*
C28	790	*10*	1735	*14*	4911	*6*	1137	*113*	852	*5*	1715	*7*	4958	*4*	394	*42*	2413	*3*	−2097	*3*	8639	*2*	248	*18*
C29	−1902	*7*	3629	*6*	559	*4*	641	*56*	−1837	*4*	3623	*5*	584	*3*	271	*32*	−3224	*3*	5335	*4*	10027	*2*	307	*20*

Table 2. *Atomic coordinates and isotropic temperature factors* ($\cdot 10^3$) *for the hydrogen atoms in the low temperature crystal structures of* **1** *(A) and* **2** *(B)*. Note that standard deviations in the coordinates may be underestimated due to distance constraints during the refinement (see text in experimental section)

	A								B							
Atom	X/a		Y/b		Z/c		Uiso		X/a		Y/b		Z/c		Uiso	
H –C3	–294	*5*	101	*3*	–159	*4*	0	*24*	–245	*2*	526	*1*	808	*1*	18	*8*
H –C5	–52	*3*	99	*4*	–29	*3*	0	*11*	–147	*2*	381	*3*	993	*2*	22	*8*
H –N11	–32	*4*	61	*4*	153	*3*	22	*14*	–36	*3*	145	*3*	971	*2*	28	*9*
H1–C13	–264	*5*	306	*4*	–288	*2*	54	*17*	–449	*3*	493	*4*	706	*1*	55	*12*
H2–C13	–176	*2*	371	*5*	–201	*3*	73	*20*	–432	*2*	628	*1*	756	*2*	33	*9*
H3–C13	–303	*5*	428	*2*	–249	*4*	58	*21*	–550	*1*	543	*3*	751	*2*	43	*10*
H1–C14	–500	*5*	234	*5*	–205	*3*	65	*20*	–465	*3*	261	*3*	767	*1*	51	*11*
H2–C14	–461	*4*	224	*4*	–294	*2*	40	*16*	–552	*1*	324	*3*	816	*2*	35	*9*
H3–C14	–489	*4*	346	*2*	–258	*3*	35	*16*	–430	*2*	248	*3*	851	*1*	34	*9*
H1–C15	–159	*8*	160	*6*	–200	*7*	211	*53*	–150	*1*	311	*3*	798	*2*	41	*10*
H2–C15	–182	*9*	38	*6*	–148	*6*	229	*50*	–272	*2*	237	*1*	783	*1*	10	*7*
H1–C19	–420	*5*	–125	*4*	–362	*4*	68	*22*	–222	*1*	340	*3*	577	*2*	33	*10*
H2–C19	–508	*4*	–128	*4*	–302	*3*	50	*18*	–335	*3*	406	*2*	581	*2*	76	*15*
H3–C19	–526	*4*	–25	*4*	–366	*4*	94	*25*	–335	*3*	230	*3*	562	*2*	74	*14*
H1–C20	69	*3*	357	*4*	0	*1*	30	*14*	89	*1*	564	*3*	848	*2*	31	*9*
H2–C20	102	*5*	437	*2*	87	*3*	47	*17*	–29	*3*	515	*4*	796	*1*	68	*13*
H3–C20	209	*1*	375	*4*	75	*3*	32	*14*	–30	*3*	587	*3*	872	*2*	57	*12*
H1–C21	214	*4*	407	*2*	279	*3*	44	*16*	196	*3*	253	*3*	789	*1*	33	*9*
H2–C21	283	*5*	301	*5*	334	*2*	69	*20*	284	*2*	271	*4*	860	*2*	68	*13*
H3–C21	313	*3*	347	*4*	252	*3*	55	*17*	223	*3*	403	*1*	824	*2*	57	*12*
H1–C26	233	*5*	–13	*5*	560	*1*	53	*19*	422	*2*	–203	*2*	981	*1*	25	*8*
H2–C26	269	*3*	–25	*3*	469	*3*	12	*12*	303	*2*	–157	*3*	1005	*1*	30	*9*
H3–C26	130	*3*	–39	*4*	462	*3*	47	*19*	402	*2*	–46	*2*	999	*1*	25	*8*
H1–C27	317	*4*	168	*4*	599	*1*	35	*15*	462	*2*	–134	*2*	860	*1*	13	*7*
H2–C27	302	*4*	267	*1*	520	*3*	26	*15*	456	*2*	23	*2*	886	*1*	36	*10*
H3–C27	373	*3*	159	*4*	515	*3*	27	*15*	374	*2*	–23	*3*	814	*1*	34	*9*
H1–C28	90	*5*	153	*5*	558	*1*	53	*18*	290	*2*	–293	*2*	861	*1*	26	*9*
H2–C28	8	*2*	139	*4*	455	*3*	43	*16*	206	*3*	–174	*3*	817	*1*	47	*11*
H3–C28	78	*5*	255	*1*	489	*4*	39	*19*	181	*2*	–235	*3*	892	*1*	16	*7*
H1–C29	–172	*4*	307	*3*	108	*2*	35	*16*	–251	*2*	590	*3*	1013	*2*	44	*10*
H2–C29	–114	*3*	414	*3*	72	*3*	49	*17*	–338	*3*	450	*2*	1030	*2*	71	*14*
H3–C29	–252	*3*	410	*3*	59	*3*	27	*13*	–388	*2*	597	*3*	1006	*2*	54	*11*

hypothesis. Although this cannot be taken as a proof for rigidity, it does make the existence of large relative vibrations between the two molecular fragments improbable.

We refrain from giving the analogous analysis for the u_{ij}'s of structure **2**, since essentially the same result is obtained: again, there is evidence for internal flexibility of the pyrrolidine ring, while no indication for vibrations between pyrrole ring and the planar part of the pyrrolidine ring is obtained.

Table 3. *Anisotropic temperature coefficients* $(\cdot\,10^4$, *in* $Å^2)$ *for non-H atoms in the low-temperature crystal structurs of* **1** *(A) and* **2** *(B)*. The temperature factor has the form: $T = \exp(-2\pi^2(h^2a^{*2}u_{11} + \ldots + 2hka^*b^*u_{12} + \ldots))$

	A						B					
Atom	u11	u22	u33	u12	u13	u23	u11	u22	u33	u12	u13	u23
C1	197 *25*	291 *32*	217 *28*	1 *25*	43 *22*	−41 *25*	207 *15*	256 *18*	283 *17*	48 *13*	73 *13*	80 *15*
C2	210 *27*	334 *33*	201 *28*	98 *25*	2 *22*	−52 *26*	129 *13*	320 *18*	219 *16*	12 *14*	21 *12*	44 *14*
C3	421 *36*	442 *45*	288 *31*	235 *35*	−153 *27*	−206 *32*	178 *14*	245 *17*	206 *16*	−21 *13*	42 *13*	15 *14*
C4	247 *27*	311 *32*	161 *27*	53 *26*	28 *22*	−52 *24*	157 *13*	194 *15*	198 *15*	−17 *12*	44 *12*	13 *13*
C5	295 *29*	233 *31*	215 *28*	79 *26*	64 *23*	−28 *26*	238 *15*	225 *17*	129 *14*	4 *13*	21 *12*	34 *13*
C6	171 *25*	248 *29*	200 *26*	39 *23*	46 *21*	13 *23*	186 *14*	214 *16*	134 *14*	4 *13*	−23 *11*	4 *13*
C7	191 *26*	245 *30*	238 *28*	−29 *24*	62 *22*	29 *25*	191 *14*	226 *16*	178 *15*	−24 *13*	10 *12*	26 *13*
C8	132 *22*	219 *30*	197 *26*	0 *22*	50 *20*	11 *23*	158 *13*	255 *17*	148 *14*	−42 *13*	10 *11*	−7 *13*
C9	128 *23*	233 *29*	209 *27*	−18 *23*	11 *21*	−31 *24*	138 *13*	223 *16*	118 *14*	−14 *12*	18 *11*	−5 *12*
N10	236 *23*	260 *25*	165 *22*	36 *21*	37 *19*	−74 *20*	224 *13*	238 *14*	195 *13*	38 *11*	44 *11*	13 *11*
N11	152 *22*	238 *26*	205 *23*	−16 *19*	−14 *18*	9 *21*	154 *11*	224 *14*	162 *13*	−11 *11*	45 *10*	42 *11*
O12	276 *19*	262 *21*	286 *19*	67 *17*	80 *16*	−24 *17*	274 *11*	454 *15*	377 *14*	146 *11*	89 *11*	80 *12*
C13	362 *35*	762 *53*	283 *32*	−71 *38*	168 *29*	−185 *36*	209 *15*	473 *24*	337 *20*	21 *17*	−10 *15*	115 *19*
C14	229 *28*	311 *35*	389 *35*	37 *27*	−60 *26*	−77 *30*	221 *16*	337 *21*	403 *21*	−44 *16*	62 *16*	30 *18*
C15	644 *49*	526 *50*	485 *42*	46 *43*	47 *38*	−154 *40*	235 *16*	252 *18*	244 *16*	25 *14*	39 *13*	16 *14*
C16	418 *36*	167 *32*	400 *36*	95 *28*	−119 *30*	−71 *29*	278 *17*	283 *19*	284 *18*	24 *15*	40 *14*	−27 *16*
O17	594 *29*	377 *27*	539 *29*	−66 *23*	193 *25*	−89 *24*	539 *16*	333 *14*	359 *14*	−71 *13*	117 *12*	41 *12*
O18	786 *31*	368 *26*	213 *20*	99 *24*	99 *21*	8 *19*	505 *15*	283 *13*	224 *12*	31 *12*	−46 *11*	8 *11*
C19	341 *36*	408 *42*	584 *44*	−93 *33*	82 *34*	88 *37*	821 *33*	404 *27*	199 *19*	−34 *25*	19 *21*	20 *18*
C20	367 *32*	390 *36*	188 *27*	−88 *31*	75 *25*	34 *28*	285 *17*	265 *20*	388 *21*	−9 *16*	81 *16*	93 *17*
C21	271 *29*	356 *36*	263 *29*	−104 *28*	27 *24*	17 *28*	271 *17*	306 *20*	340 *20*	−49 *16*	156 *15*	50 *17*
C22	220 *26*	222 *30*	183 *26*	61 *25*	40 *22*	18 *24*	153 *13*	272 *17*	123 *13*	−29 *13*	26 *11*	−22 *13*
O23	288 *21*	279 *22*	217 *19*	−74 *18*	29 *17*	51 *17*	218 *11*	266 *12*	233 *11*	24 *10*	98 *9*	87 *10*
O24	255 *19*	213 *20*	140 *17*	−23 *17*	18 *15*	35 *16*	177 *10*	214 *11*	236 *11*	44 *9*	77 *9*	46 *9*
C25	242 *28*	299 *33*	131 *25*	17 *24*	51 *22*	56 *23*	161 *14*	235 *17*	264 *16*	43 *13*	58 *13*	25 *14*
C26	419 *37*	268 *35*	241 *32*	−34 *30*	63 *29*	93 *27*	204 *16*	336 *20*	246 *17*	28 *15*	−11 *14*	44 *16*
C27	307 *32*	452 *42*	170 *29*	−65 *32*	30 *26*	−4 *30*	207 *16*	326 *21*	356 *20*	34 *16*	94 *15*	41 *17*
C28	315 *34*	630 *51*	227 *32*	118 *36*	82 *27*	25 *34*	214 *15*	273 *19*	269 *18*	16 *15*	79 *14*	−49 *16*
C29	233 *27*	365 *35*	183 *26*	54 *26*	34 *22*	−43 *25*	325 *18*	359 *22*	260 *18*	52 *17*	113 *15*	−14 *16*

Table 4. *Summary of experimental conditions*

		1 (low temp.)	**1** (room temp.)	**2** (low temp.)
chemical formula		$C_{22}H_{32}N_2O_5$		$C_{22}H_{32}N_2O_5$
crystal size [mm]		.1 × .25 × .3	.15 × .3 × .3	.2 × .25 × .45
temperature [K] (cold stream)		93 ± 1	293 ± 2	93 ± 1
space group		$P2_1/a$		$P2_1/n$
cell dimensions	a [Å]	12.019 (4)	12.132 (3)	11.830 (2)
	b [Å]	12.073 (4)	12.228 (4)	9.739 (1)
	c [Å]	16.070 (3)	16.250 (4)	19.483 (4)
	β [°]	110.61 (3)	111.08 (2)	100.28 (1)
	V [$Å^3$]	2182.6	2249.2	2208.8
number of molecules per unit cell		4		4
calculated density [$g\,cm^{-3}$]		1.231	1.194	1.216
number and θ-range [°] of reflections used to refine cell constants		15 $24 \leqslant 2\theta \leqslant 30$	14 $14 \leqslant 2\theta \leqslant 32$	23 $19 \leqslant 2\theta \leqslant 21$
limits for data collection [°]		$0 \leqslant 2\theta \leqslant 60$ $- \leqslant 16\ h \leqslant 16$ $0 \leqslant k \leqslant 16$ $0 \leqslant l \leqslant 22$	$0 \leqslant 2\theta \leqslant 50$ $0 \leqslant h \leqslant 14$ $0 \leqslant k \leqslant 14$ $-19 \leqslant l \leqslant 18$	$0 \leqslant 2\theta \leqslant 60$ $-18 \leqslant h \leqslant 18$ $0 \leqslant k \leqslant 15$ $0 \leqslant l \leqslant 27$
scan width [°] (ω/θ-scan)		$\Delta\omega = 1.2$	$\Delta\omega = 1.2$	$\Delta\omega = 1.2$
number/frequency of standard refs.		3/100	3/100	3/100
max. variation of standard intensities		± 2%	± 3%	± 3%
number of observed reflections		7061	4525	7214
number of independent reflections		6357	3973	6451
number of reflections with $\lvert F_o \rvert > 4\sigma(F_o)$		1994	1218	2675
R/R_w-factors		0.070/0.067	0.063/0.062	0.055/0.052
number of parameters		391	294	391
number of observations (including distance constraints)		2024	1218	2705
coefficients a/b of weighting system $w_i = a/(\sigma(F_i)^2 + b F_i^2)$		2.40/0.00035	2.13/0.0004	1.69/0.00007
highest peak/lowest trough in final ΔF-Fourier synthesis [$e A^{-3}$]		0.63/− 0.46	0.27/− 0.21	0.30/− 0.29

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Experimental

Colourless crystals of **1** and **2** were obtained by dissolving a small amount of material[2] in about 1 ml chloroform. The solution was placed inside a dessiccator containing a second open beaker with *n*-hexane and kept in the coldroom for several weeks. The crystals used for structure analysis had to be cut with a razor blade from larger lumps containing several crystals.

All X-ray work was carried out on an extensively modified STOE 4-circle diffractometer (MoK_α-radiation, graphite monochromator, $\lambda = 0.71069$ Å) equipped with a NONIUS low-temperature attachment. To prevent deposition of ice on the crystal, the diffractometer was placed inside a glove box. Conditions of data collection and structure refinement are summarized in Table 4.

Data processing involved the usual LP-corrections, but neither absorption- nor extinction correction [($\mu(MoK_\alpha) = 0.94\,cm^{-1}$ for **1** and $0.93\,cm^{-1}$ for **2**)]. The two structures were solved by direct methods and refined first by full matrix and subsequently by blocked least-squares techniques. In view of their superior quality, the refinement was first carried out for the two low-temperature data sets, applying the following conditions: all non-hydrogen atoms were refined with anisotropic temperature factors, H-atoms were included at observed positions and refined with isotropic temperature factors. In the terminal refinement cycles, aliphatic C–H distances were constrained to assume the same value; this "average" aliphatic C–H dustance converged to 1.00 Å in both low-temperature refinements.

Subsequently, the low-temperature coordinates were used as a starting point for the refinement of **1** against the room-temperature data. Again, all non-H atoms were refined with anisotropic temperature factors, whereas hydrogen atoms were kept at the positions of the low-temperature refinement. An isotropic temperature factor was refined for each H-atom.

Atomic scattering factors were from the International Tables[13]. Computer programs used (in locally modified versions) are summarized in Ref.[14].

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