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On the Molecular Structure of the Phytochrome Chromophore: X-Ray Analysis of Two 2,3-Dihydrobilatriene-abc Derivatives*

Christoph Kratky[a,*], **Heinz Falk**[b], **Karl Grubmayr**[b], and **Ulrich Zrunek**[b]

[a] Institut für Physikalische Chemie, Universität Graz, A-8010 Graz, Austria
[b] Institut für Analytische, Organische und Physikalische Chemie, Johannes-Kepler-Universität Linz, A-4040 Linz, Austria

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The molecular and crystal structures of the two 2,3-dihydrobilatrienes-abc **1** and **2**, representing model compounds for the phytochrome chromophore, were determined by X-ray crystallography at 97 K. Crystals of the racemate **1** contain disordered regions. Both molecules are found to be of *all*-(*Z*) configuration, assuming a helical conformation. The acidic hydrogen atoms are localized at the nitrogen atoms of rings A, C and D. A summary of the geometries of unsaturated five-membered rings as observed in four accurate low-temperature crystal structures of bilatrienes-abc is given.

(Keywords: Crystal structure of dihydrobilatriene-abc; Dihydrobilatriene-abc; Molecular geometry of dihydrobilatriene-abc; Phytochrome model compounds)

Zur molekularen Struktur des Phytochromchromophors: Röntgenstrukturanalyse zweier 2,3-Dihydrobilatrien-abc-Derivate

Die Molekül- und Kristallstruktur der beiden 2,3-Dihydrobilatriene-abc **1** und **2**, welche Modelle für den Phytochromchromophor repräsentieren, wurden mittels Röntgenkristallstrukturanalyse bei 97 K bestimmt. Die Kristalle des Racemats **1** enthalten ungeordnete Bereiche. Die beiden Moleküle besitzen *all*-(*Z*) Konfiguration und liegen im Kristall in helikaler Konformation vor. Die aciden Wasserstoffatome sind jeweils an den Stickstoffatomen der Ringe A, C und D lokalisiert. Die in genauen Tieftemperatur-Kristallstrukturen von vier Bilatrien-abc Derivaten beobachteten molekularen Geometrien der ungesättigten Heterocyclenringe werden zusammengefaßt.

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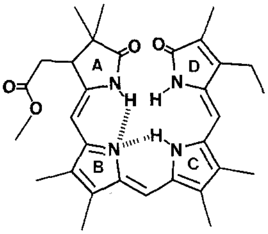
Introduction

Phytochromobilin, the chromophore molecule of the plant pigment phytochrome[1], is a linear tetrapyrrole of the 2,3-dihydrobilatriene-abc type. Although the details of its biochemical function are far from being understood, the 2,3-dihydrobilatriene-abc chromophore has recently received much attention, and much is known about its chemical properties as far as tautomeric preferences[2–4], diastereomeric forms[5,6], and reactivity[7] is concerned. However, to our knowledge[8], with the exception of the two diastereomeric 3-oxo-2,3-dihydrobilatrienes **3** and **4**[9], no crystal structure analysis of this type of chromophore has been reported so far.



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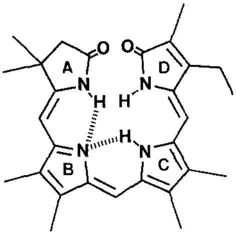

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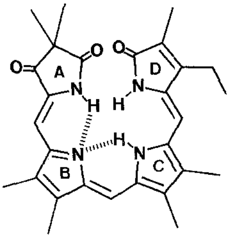

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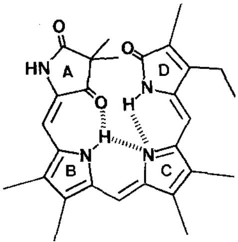

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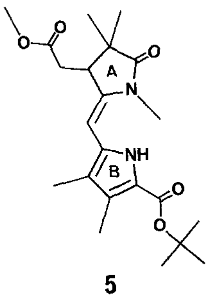

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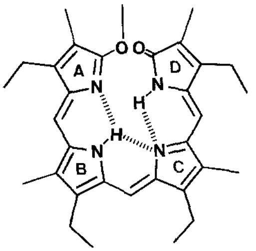

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In the present communication, we describe the crystal structures of compounds **1** and **2**. The structure determination of **2** was undertaken after it had turned out that the crystal structure of **1** contains disordered regions. Both structures were determined at low temperature to optimize accuracy and reliability. An analysis of the temperature factors following the method outlined in a preceding communication[10] will also be described for compound **2**, and the geometrics of unsaturated five membered rings found in bilatrienrs-abc will be discussed.

Results and Discussion

Atomic coordinates and temperature coefficients as observed in the low-temperature crystal structures of **1** and **2** are given in Tables 1–4. Fig. 1 shows ORTEP-projections of the two molecules into a mean plane through all atoms of the bilatriene system; views perpendicular to this plane, in the direction of the C9–C11 vector, are shown in Fig. 2.

Partial disorder is observed in the crystal structure of **2**, notably of the ring A substituents and of the solvated chloroform molecule. Therefore, with the exception of the three N–H protons, we did not attempt to observe H-atoms, and we also refrain from a detailed discussion of the bonding geometry for this compound. The structure of **2**, on the other hand, is of high quality, which is manifested in a low residual (see Table 6) and in the fact, that all hydrogen atoms could be observed in difference *Fourier* syntheses and behaved well during least-squares refinement. The bond lengths, bond angles and a few torsion angles for the tetrapyrrolic moiety as observed in the crystal of **2** are shown in Fig. 3, which also defines the atom numbering used for the description of the crystal structure.

Both molecules assume an overall helical conformation, which has been observed for all known crystal structures of verdinoid compounds[8]. The "helix pitch" (distance between carbonyl oxygen atoms on rings A and D) is also quite in the range of what is observed in related compounds[8] (**1**: 3.55 Å; **2**: 3.47 Å).

Tautomerism, Hydrogen Bonding and Crystal Packing

The tautomeric form of 2,3-dihydrobilatrienes was determined using a combination of NMR and UV/VIS techniques[3]. Thus, in aqueous solution, three protons are bonded to the nitrogens of rings A, C and D, with the proton on the saturated ring A being the most acidic one[11].

The crystal structure analyses are in full agreement with the distribution of the acidic protons observed in solution: in both structures, the inner protons could be observed in difference *Fourier* syntheses and refined to a reasonable streochemistry (Fig. 3): they are attached to atoms

Table 1. *Atomic coordinates and (equivalent) isotropic temperature factors* ($\cdot 10^3$, *U-values in* Å^2) *for the crystal structure of* **1**. E.s.d.'s are given in italics. The equivalent isotropic temperature factor was obtained as one third of the trace of the orthoganlized U_{ij} tensor, and it corresponds to an isotropic temperature factor of the form $T = \exp(-8\pi^2 \cdot u \cdot \sin^2 \vartheta/\lambda^2)$

Atom	X/a		Y/b		Z/c		Uiso	
C1	256	*3*	−125	*2*	248	*2*	34	*8*
C2	319	*3*	−208	*2*	336	*2*	4	*2*
C3	451	*4*	−157	*3*	333	*4*	8	*3*
C4	430	*3*	−37	*2*	270	*2*	22	*7*
C5	495	*3*	51	*2*	274	*2*	19	*7*
C6	461	*2*	167	*2*	218	*2*	10	*6*
C7	505	*2*	258	*2*	248	*2*	15	*6*
C8	447	*3*	353	*2*	181	*2*	21	*7*
C9	360	*2*	317	*2*	122	*2*	15	*6*
C10	293	*3*	387	*2*	44	*2*	16	*7*
C11	229	*2*	350	*2*	−21	*2*	4	*5*
C12	139	*2*	406	*2*	−98	*2*	8	*6*
C13	96	*2*	333	*2*	−139	*2*	7	*6*
C14	164	*2*	231	*2*	−93	*2*	7	*6*
C15	138	*2*	134	*2*	−110	*2*	9	*6*
C16	210	*3*	32	*2*	−81	*2*	17	*7*
C17	172	*2*	−76	*2*	−82	*2*	8	*6*
C18	262	*2*	−155	*2*	−30	*2*	7	*6*
C19	360	*2*	−100	*2*	4	*2*	0	*5*
N20	318	*2*	−25	*2*	221	*2*	19	*6*
H-N20	281	*19*	38	*16*	188	*16*	0	*56*
N21	380	*2*	198	*1*	148	*1*	7	*4*
N22	236	*2*	246	*1*	−23	*2*	6	*5*
H-N22	297	*19*	186	*15*	15	*15*	0	*55*
N23	322	*2*	12	*2*	−27	*2*	20	*6*
H-N23	374	*19*	59	*16*	−21	*15*	3	*60*
O24	152	*2*	−130	*1*	214	*1*	26	*5*
C25	233	*4*	−212	*3*	438	*3*	6	*3*
C26	331	*3*	−320	*2*	312	*3*	4	*2*
C27	567	*4*	−200	*3*	312	*4*	13	*4*
C28	605	*3*	−315	*3*	395	*4*	7	*3*
O29	575	*2*	−354	*2*	483	*2*	5	*2*
O30	669	*2*	−376	*2*	332	*2*	5	*2*
C31	705	*4*	−496	*3*	389	*3*	6	*3*
C32	606	*3*	249	*2*	329	*2*	29	*8*
C33	446	*2*	471	*2*	183	*2*	7	*6*
C34	102	*3*	542	*2*	−128	*2*	19	*7*
C35	−2	*2*	365	*2*	−219	*2*	5	*6*
C36	50	*2*	−91	*2*	−128	*2*	11	*6*
C37	87	*3*	−50	*3*	−253	*3*	40	*9*
C38	267	*3*	−283	*2*	−4	*2*	15	*6*
O39	459	*1*	−146	*1*	51	*1*	2	*4*
C40*	818	*5*	−269	*4*	580	*6*	16	*6*
CL41*	903	*2*	−276	*2*	672	*1*	12	*2*
CL42*	755	*4*	−102	*2*	525	*2*	14	*3*
CL43*	892	*2*	−272	*2*	449	*2*	11	*2*
CL44*	−102	*3*	617	*3*	−441	*4*	16	*4*
CL45*	−202	*5*	844	*3*	−492	*5*	18	*6*

Table 2. *Coordinates and temperature coefficients (· 10^4) for the non-hydrogen atoms in the structure of* **2**

Atom	X/a		Y/b		Z/c		Uiso	
C1	6728	*5*	2889	*7*	5708	*3*	204	*45*
C2	6287	*7*	4008	*8*	5289	*3*	292	*54*
C3	6670	*5*	3769	*7*	4716	*3*	207	*45*
C4	7168	*5*	2413	*7*	4825	*3*	174	*42*
C5	7593	*6*	1748	*7*	4442	*3*	179	*45*
C6	8118	*5*	476	*7*	4569	*3*	159	*41*
C7	8794	*5*	−108	*7*	4207	*3*	178	*44*
C8	9162	*5*	−1238	*7*	4461	*3*	172	*43*
C9	8698	*5*	−1383	*7*	4975	*3*	151	*41*
C10	8809	*6*	−2444	*8*	5342	*3*	186	*43*
C11	8271	*5*	−2669	*6*	5804	*3*	123	*40*
C12	8434	*5*	−3667	*7*	6231	*3*	139	*40*
C13	7709	*5*	−3436	*7*	6587	*3*	149	*43*
C14	7108	*5*	−2326	*7*	6367	*3*	146	*41*
C15	6330	*6*	−1660	*7*	6612	*3*	147	*45*
C16	5631	*5*	−709	*7*	6378	*3*	131	*42*
C17	4978	*5*	77	*7*	6689	*3*	151	*42*
C18	4474	*5*	997	*7*	6308	*3*	139	*40*
C19	4746	*5*	837	*7*	5741	*3*	177	*43*
N20	7176	*5*	2023	*6*	5394	*2*	199	*38*
N21	8065	*4*	−275	*5*	5032	*2*	155	*33*
N22	7454	*4*	−1881	*5*	5887	*2*	162	*35*
N23	5480	*4*	−191	*5*	5805	*2*	158	*32*
O24	6705	*4*	2779	*5*	6235	*2*	300	*32*
C25	7538	*7*	4745	*8*	4667	*4*	361	*58*
C26	5740	*7*	3846	*8*	4139	*4*	363	*57*
C27	9013	*7*	518	*8*	3659	*3*	227	*48*
C28	9855	*6*	−2229	*8*	4272	*3*	228	*49*
C29	9218	*6*	−4750	*7*	6304	*3*	187	*46*
C30	7626	*6*	−4258	*7*	7112	*3*	203	*48*
C31	4940	*6*	−207	*7*	7314	*3*	201	*45*
C32	4209	*6*	−1367	*7*	7357	*3*	209	*47*
C33	3727	*6*	2072	*7*	6386	*3*	230	*48*
O34	4418	*3*	1469	*4*	5270	*2*	207	*29*
C35*	8311	*6*	1493	*8*	7297	*3*	359	*53*
CL36*	7664	*2*	1064	*2*	7945	*1*	373	*13*
CL37*	9426	*2*	2553	*2*	7486	*1*	390	*13*
CL38*	8647	*2*	119	*2*	6947	*1*	630	*17*

N 20, N 22 and N 23, and two intramolecular hydrogen bonds are formed with the imino nitrogen atom N 21 as acceptor.

Fig. 4 shows packing diagrams for the two crystal structures. Although the two compounds crystallize in different spacegroups and the packing diagrams look considerably different, the pattern of intermolecular H-bonds is quite similar: in both compounds, the ring D proton forms a H-bond to the ring D carbonyl group of a centrosymmetrically related molecule (**1**: H 23 ... O $39_{1-x,-y,-z}$, 2.03 Å; **2**: H 23 ... O $34_{1-x,-y,1-z}$, 1.83 Å). A weaker H-bonding interaction appears to exist between H 22

Table 3. *Coordinates and isotropic temperature coefficients* $(\cdot 10^3)$ *for the* H-*atoms in the crystal structure of* **2**. Note that positional e.s.d's may be underestimated as a result of distance constraints (see text in experimental section)

Atom	X/a		Y/b		Z/c		Uiso	
H1–C2	643	*6*	499	*3*	546	*3*	43	*27*
H2–C2	543	*2*	390	*7*	525	*3*	72	*24*
H –C5	763	*6*	208	*7*	404	*3*	65	*25*
H –C10	929	*5*	–312	*6*	530	*2*	14	*18*
H –C15	630	*5*	–195	*6*	697	*3*	8	*17*
H –N20	750	*6*	125	*8*	555	*3*	34	*23*
H –N22	724	*4*	–123	*6*	565	*2*	16	*18*
H –N23	553	*7*	–53	*8*	539	*4*	70	*30*
H1–C25	788	*5*	460	*7*	428	*2*	36	*22*
H2–C25	823	*3*	472	*7*	506	*2*	46	*24*
H3–C25	724	*5*	574	*2*	466	*3*	18	*20*
H1–C26	604	*5*	362	*7*	375	*2*	39	*24*
H2–C26	530	*6*	475	*4*	404	*4*	72	*29*
H3–C26	506	*4*	326	*6*	420	*3*	56	*28*
H1–C27	826	*3*	77	*6*	334	*2*	28	*19*
H2–C27	938	*5*	148	*3*	375	*3*	29	*21*
H3–C27	955	*4*	9	*6*	342	*2*	50	*20*
H1–C28	1025	*5*	–179	*7*	395	*3*	91	*26*
H2–C28	943	*4*	–313	*3*	413	*2*	33	*19*
H3–C28	1055	*4*	–255	*8*	462	*3*	88	*32*
H1–C29	881	*5*	–569	*3*	622	*3*	62	*24*
H2–C29	968	*4*	–482	*6*	677	*1*	9	*17*
H3–C29	968	*5*	–476	*7*	597	*2*	37	*24*
H1–C30	745	*5*	–358	*5*	744	*2*	55	*21*
H2–C30	724	*12*	–519	*9*	695	*6*	272	*89*
H3–C30	837	*3*	–455	*7*	743	*2*	45	*25*
H1–C31	572	*2*	–33	*6*	763	*2*	18	*18*
H2–C31	470	*4*	63	*3*	754	*2*	8	*17*
H1–C32	419	*4*	–158	*5*	781	*1*	14	*16*
H2–C32	448	*5*	–230	*3*	722	*3*	42	*22*
H3–C32	337	*2*	–121	*6*	712	*2*	41	*20*
H1–C33	406	*4*	300	*3*	630	*2*	19	*17*
H2–C33	354	*5*	212	*7*	682	*1*	34	*24*
H3–C33	296	*3*	215	*6*	605	*2*	54	*19*
H –C35*	759	*7*	181	*9*	694	*4*	106	*36*

and the symmetry related ring D carbonyl oxygen atom (of length 2.55 Å in **1** and 2.60 Å in **2**). This pattern of intermolecular H-bonds leads to the same type of centrosymmetric dimer as observed in the (*Z*)-isomer of the 3-oxo-2,3-dihydrobilatriene **3** described in the preceding communication[9].

In **2**, the solvated chloroform molecule is H-bonded to the ring A carbonyl oxygen (H–C35...O24, 1.95 Å). In **1**, the chloroform molecule is disordered, prohibiting localisation of its proton. However, judging from the packing diagram (Fig. 4), it is probable that the chloroform is hydrogen-bonded to the ester carbonyl oxygen atom O 29.

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

Atom	u11	u22	u33	u12	u13	u23
C1	149 *43*	249 *48*	221 *39*	−9 *38*	61 *35*	−67 *35*
C2	365 *57*	188 *50*	312 *46*	−25 *48*	67 *44*	−73 *41*
C3	181 *44*	173 *45*	256 *40*	−125 *39*	34 *35*	−34 *36*
C4	218 *43*	139 *42*	153 *35*	−20 *39*	26 *33*	−10 *36*
C5	361 *50*	103 *42*	116 *37*	−37 *39*	138 *37*	57 *34*
C6	204 *43*	122 *40*	135 *35*	−74 *37*	14 *34*	−41 *32*
C7	163 *43*	199 *46*	174 *37*	−120 *39*	48 *34*	−34 *35*
C8	192 *44*	211 *45*	79 *34*	−33 *38*	−29 *33*	−1 *34*
C9	178 *42*	120 *41*	154 *36*	−60 *35*	38 *32*	−23 *33*
C10	207 *44*	173 *43*	179 *37*	1 *41*	52 *35*	−52 *38*
C11	225 *43*	32 *39*	116 *33*	−47 *35*	51 *33*	−47 *32*
C12	132 *41*	103 *39*	179 *36*	−19 *36*	33 *33*	−34 *32*
C13	166 *44*	150 *42*	124 *37*	7 *37*	23 *34*	16 *32*
C14	139 *41*	134 *42*	177 *35*	−59 *38*	61 *34*	−7 *35*
C15	177 *46*	185 *45*	103 *38*	−49 *38*	78 *36*	26 *35*
C16	59 *39*	157 *43*	182 *38*	22 *35*	39 *33*	22 *33*
C17	109 *42*	202 *45*	124 *34*	−43 *38*	−2 *32*	28 *34*
C18	152 *40*	145 *40*	117 *35*	5 *38*	28 *32*	−42 *34*
C19	95 *41*	193 *44*	227 *39*	−44 *36*	11 *35*	−34 *35*
N20	195 *38*	202 *38*	188 *32*	52 *31*	27 *29*	38 *28*
N21	116 *33*	175 *33*	178 *28*	−49 *28*	42 *26*	−65 *27*
N22	166 *35*	148 *34*	183 *31*	44 *29*	67 *28*	27 *28*
N23	208 *33*	175 *32*	97 *28*	38 *29*	49 *26*	−22 *27*
O24	297 *31*	383 *34*	214 *26*	44 *28*	52 *25*	−26 *25*
C25	420 *60*	308 *54*	399 *52*	117 *50*	186 *47*	−44 *47*
C26	377 *59*	230 *52*	403 *52*	184 *50*	−45 *46*	−29 *45*
C27	298 *50*	221 *47*	180 *40*	26 *42*	96 *38*	56 *37*
C28	236 *49*	252 *49*	257 *43*	−58 *40*	173 *40*	−90 *38*
C29	141 *45*	245 *47*	177 *39*	49 *39*	44 *34*	22 *37*
C30	190 *47*	220 *49*	222 *42*	58 *41*	96 *38*	16 *37*
C31	231 *46*	192 *44*	206 *39*	43 *42*	101 *38*	44 *37*
C32	301 *50*	259 *48*	84 *36*	−11 *43*	82 *37*	66 *35*
C33	217 *49*	218 *47*	266 *42*	129 *40*	82 *40*	−16 *38*
O34	237 *29*	255 *31*	122 *23*	11 *26*	34 *21*	3 *23*
C35*	242 *48*	647 *65*	192 *38*	−13 *47*	63 *37*	−183 *43*
CL36*	322 *12*	471 *14*	357 *11*	17 *12*	145 *10*	13 *11*
CL37*	618 *15*	249 *11*	335 *10*	−38 *12*	179 *11*	9 *10*
CL38*	420 *14*	653 *18*	931 *18*	−255 *14*	379 *14*	−614 *15*

Five Ring Conformation

The planarity of pyrrole and pyrrolenine rings is as found in related structures[8−10]. The deviations from a least squares plane for the pyrrolidine ring are considerably different for **1** and **2**; when expressed in terms of the established description of a pseudorotating pentagon[12], the puckering amplitude is 0.19 Å in **1** and 0.08 Å in **2**. The former value, which stems from a ring with a distribution of temperature ellipsoids

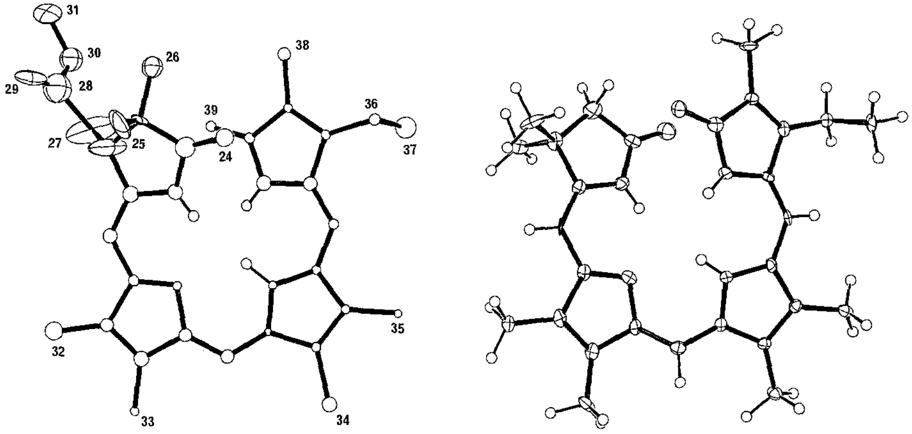


Fig. 1. ORTEP drawing (50% probability) of the tetrapyrrole moiety, projected approximately into a mean plane, as observed in the crystal structures of **1** (left, with atom numbers for the substituent atoms) and **2** (right). The radii of hydrogen atoms were arbitrarily set to 0.1 Å; note, that the radii of atoms C 19 and O 39 in **1** were also set to 0.1 Å

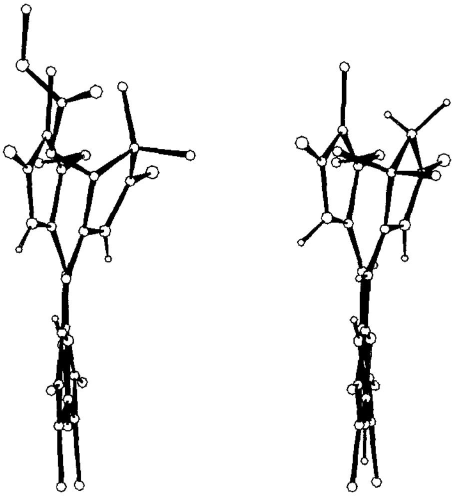


Fig. 2. Projection of **1** (left) and **2** (right) in the direction of the C 9 – C 11 vector

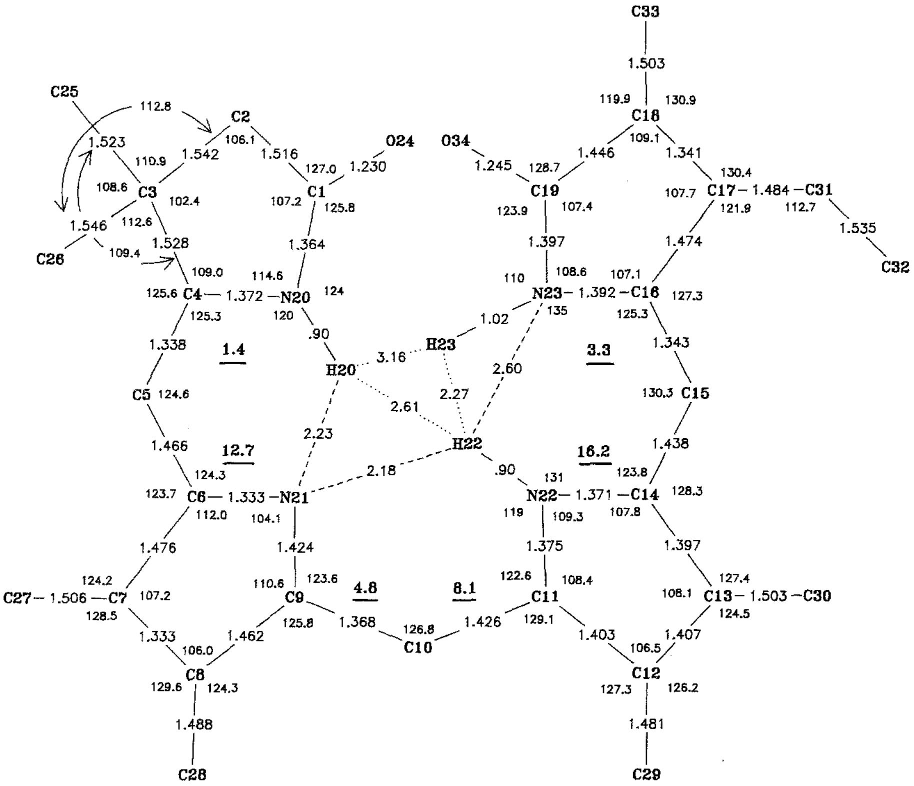


Fig. 3. Bond lengths, bond angles and $C_\alpha - C_m$ dihedral angles (underlined) from the crystal structure of **2**. Standard deviations are as follows: $X-Y$, $\sigma \sim .008 - .012$, N−H, $\sigma \sim 0.06$ Å; $X-Y-Z$, $\sigma \sim 0.4-0.7$; $X-\mathrm{N}-\mathrm{H}$, $\sigma \sim 3.6-4.2$ Å (X, Y, Z = C, N, O, Cl)

(Fig. 1) provoking the suspicion of disorder, has to be treated with caution; however, the suspected disorder is more likely to decrease the observed puckering amplitude than to increase it, so that we have to regard the value of 0.19 Å as a lower limit for the puckering amplitude of **1**.

Both values lie within the range of puckering amplitudes observed in 18 pyrrolidine rings[12,13] with exocyclic double bonds in positions 2 and 5. The difference in puckering amplitudes between the two structures are probably caused by the differences in pyrrolidine ring substitution; the value found in **1** is to be compared with values for identically substituted pyrrolidine rings in the (*E*)- and (*Z*)-isomers of **5**[10], where puckering amplitudes of 0.29 Å were observed. For the reasons outlined above, the discrepancy is not necessarily of physical significance.

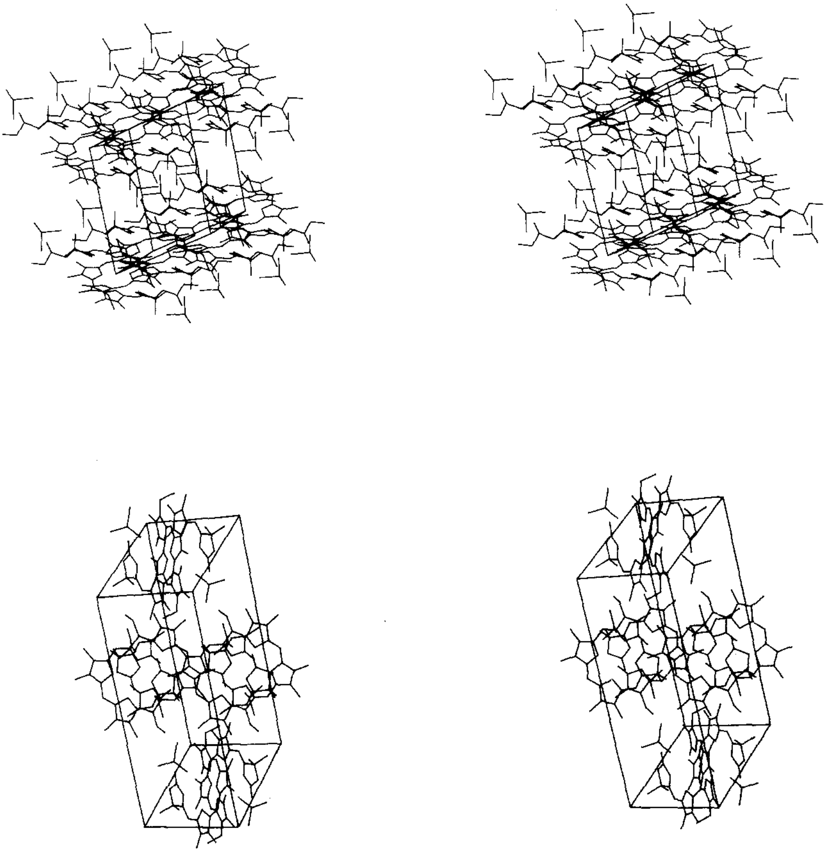


Fig. 4. Packing diagrams for **1** (top) and **2** (bottom). The orientation of crystal axes in both cases is as follows; *X* back to front; *Y* left to right; *Z* upwards

The large differences in the puckering amplitudes indicate, that (saturated) pyrrolidine rings in such compounds are instrinsically almost planar, but they can easily be deformed to considerable puckering by appropriate vicinal substitution.

Analysis of Temperature Factors

The analysis of temperature factors along the lines described previously[10] leads to a very clear-cut result when applied to the u_{ij}-values from the structure of **2**: the halve normal probability plots (Fig. 5) demonstrate, that detectable non-rigidity exists only within ring A and its substituents. It is instructive to compare the results on **2** with those

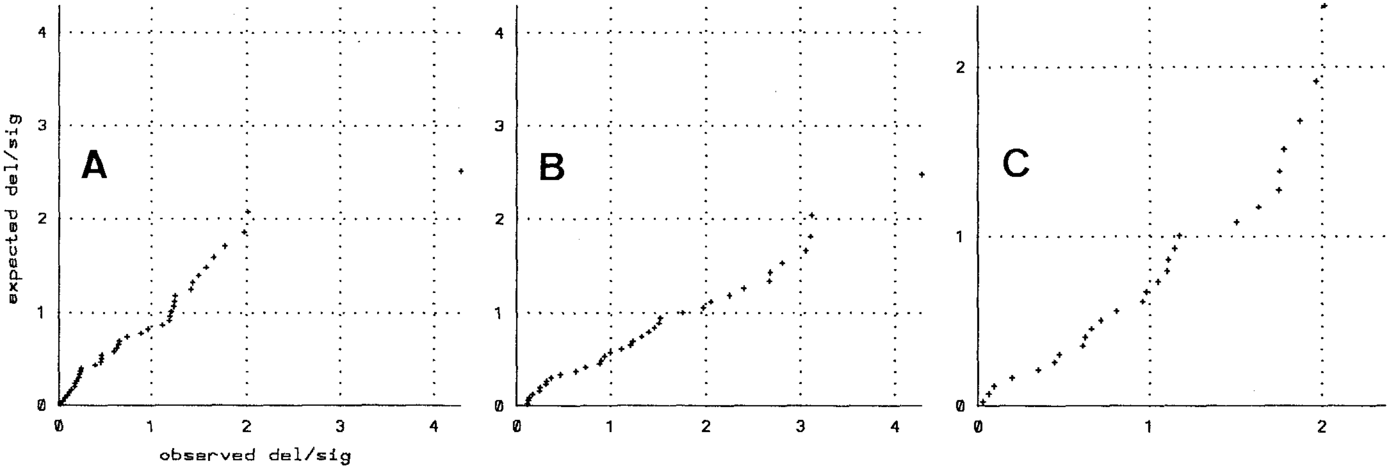


Fig. 5. Halve-normal probability plots of δ_{kl}. *A* k, l = all pairs of bonded atoms; *B* k, l = atoms C1–C5, N20, O24, C25, C26; *C* k = C1, C4, N20; l = C15–C19, N23, C31, C33

reported previously for **4** and the (*E*) and (*Z*) diastereomers of **5**: in all four compounds, the pyrrolidine rings show internal flexibility at comparable levels of significance. While, for **4**, we reported some indication for relative flexibility between rings A and D[9], no such indication can be detected for **2**. A conclusive evaluation of these results can not yet be given at this point.

Bonding Geometry in Bilatrienes

Previous high accuracy structure determinations (low temperature, all protons refined) of verdinoid compounds involved the structures of **3**[9], **4**[9] and **6**[8a]. We shall use the geometries of these three compounds and the one of **2** (Fig. 3) to analyze some aspects of the bonding geometry of bilatrienes.

A notable common feature of the three dihydrobilatrienes **2**, **3** and **4** is the fact that in all three compounds, the exocyclic double bond at ring D is longer than the one at ring A. This is somewhat in contrast to the chemical evidence, which yields a lower thermal isomerization barrier for the ring A double bond[6].

In discussing structures **3** and **4**[9], we noted the difference in tautomeric forms within the pyrromethene fragment as the dominating effect on the bonding geometry, most of which can be rationalized by considering the canonical representation of the chemical formula. The following discussion will consequently be based on a comparison of structural fragments with identical canonical formula.

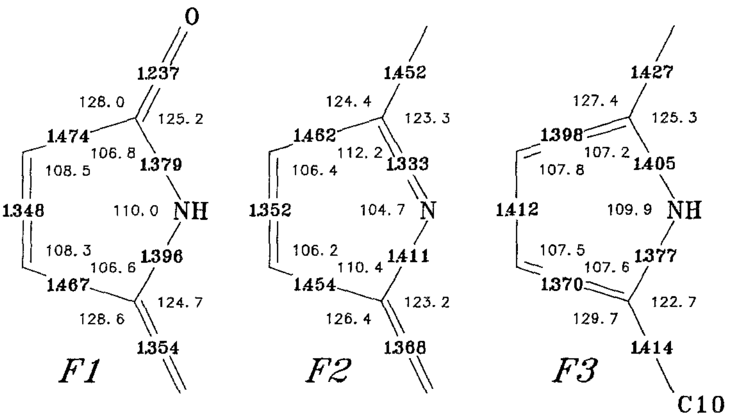
There are three different kinds of unsaturated five membered rings in the four structures, each kind of ring occurs once in each compound. The three ring types are listed in Table 5, together with a set of "best" bond lengths and -angles obtained by averaging the appropriate geometrical parameters from the four structure determinations. Ring type 1 occurs as ring D in all four compounds, whereas types 2 and 3 are found either as ring B or C; the correct identification between ring type and position in each of the four structures is also given in Table 5.

The remainder of Table 5 is devoted to root mean square deviations (r.m.s.d.'s) between bonding parameters observed in the four crystal structures and the mean values. The r.m.s.d.'s are given separately for bondlengths (BL) and bond angles (BA) within the five-membered rings (*endo*) and for parameters involving C_m atoms (*exo*).

All in all, the r.m.s.d.'s justify the classification into ring types of different canonical formula. However, several of the r.m.s.d.'s are beyond experimental error, some of which not readily interpretable. We only list a few factors influencing the molecular geometry:

Hydrogen Bonding: basically, two types of H-bonding are observed in the four structures: the pattern found in **2** and **3**, and the one found in **4**

Table 5. *Geometrical parameters for the three ring types; further explanations are given in the text*



Compound		2	3	4	6
F1	ring	*D*	*D*	*D*	*D*
BL	endo	.015	.013	.009	.008
	exo	.009	.015	.005	.015
BA	endo	.82	1.02	.81	.76
	exo	1.02	.68	1.18	.73
F2	ring	*B*	*B*	*C*	*C*
BL	endo	.012	.010	.002	.005
	exo	.010	.005	.003	.010
BA	endo	.47	.27	.51	.25
	exo	.73	.76	1.23	.42
F3	ring	*C*	*C*	*B*	*B*
BL	endo	.008	.010	.004	.005
	exo	.011	.011	.005	.004
BA	endo	.67	.66	.52	.19
	exo	.91	1.64	.83	1.39

and **6**. The two patterns differ with respect to the fate of the ring D proton, which is involved in intermolecular H-bonding in **4** and **6**. The effect on the bonding geometry of ring D is quite notable: the endocyclic ring D geometries agree well between **4** and **6**, whereas the two compounds with intermolecular H-bonds agree less well with each other and show larger deviations from the mean geometries.

Steric Effects: some geometrical consequences of steric effects were already discussed in conjunction with the structures of **3** and **4**[9]; the main effects are observed at the exocyclic bond angles and at the C_m bond angles. The effect on exocyclic bond angles is manifested by their larger r.m.s.d.'s compared with the endocyclic ones. However, exocyclic bond angles are also likely to be affected by intramolecular H-bonding, and the two effects (H-bonding and steric effects) are difficult to separate.

Rotation about Exocyclic Bonds: one might expect that an increase of the dihedral angle about one of the exocyclic bonds would be accompanied by an increase in the corresponding bondlength. Such an effect cannot be observed in the four structures. Neither do exocyclic bondlengths preferentially show larger r.m.s.d.'s than endocyclic ones, nor can one find correlations similar to the one reported for dihydropyrromethenones[10]. It is very likely that a dependence between bondlength and dihedral angle does exist for the $C_\alpha - C_m$ bonds, but in the present structures this appears to be clouded by other effects with larger geometrical consequences.

Experimental

Both compounds were crystallized from chloroform/*n*-hexane, but the procedure adopted differed slightly between the two. For **1**[2], a small amount of material (less than 1 mg) was suspended in about 1 ml of *n*-hexane. Chloroform was added until all material was dissolved. Compound **2**[11] was directly dissolved in chloroform. Both solutions were placed in a dessiccator containing *n*-hexane and left in the coldroom for several weeks, whereupon small crystals appeared.

All X-ray work was carried out on a locally modified STOE 4-circle diffractometer (MoK_α-radiation, graphite monochromator, $\lambda = 0.71069$ Å) equipped with a NONIUS low temperature attachment. The whole diffractometer is placed inside a glove box to minimize the formation of ice on the crystal. Relevant experimental conditions and a summary of the results of structure refinements are given in Table 6.

Data processing involved the usual merging of multiply recorded and symmetry-related reflections and LP-corrections. No absorption- or extinction corrections were applied [$\mu(MoK_\alpha) = 3.24\,cm^{-1}$ for **1** and $3.47\,cm^{-1}$ for **2**]. The structures were solved by direct methods and refined by least-squares techniques; in the final cycles, computer limitations forced a blocking of the least-squares matrix.

During the refinement of **1**, it soon turned out that the structure suffers from partial disorder. The small number of significant reflections prohibited the refinement of anisotropic temperature factors for all atoms; therefore, only atoms C 2, C 3, C 25–O 31 were refined anisotropically, for all other atoms, only isotropic temperature factors were determined. Non-positive definite temperature coefficients resulted for atoms C 26, C 28 and O 30. With the exception of H (N 20), H (N 22) and H (N 23), which were included at observed positions and subjected to unconstrained, isotropic refinement, no H-atoms were included. The region of the solvated chloroform molecule showed several residual peaks, indicating considerable disorder. After numerous attempts to explain the electron density in this region in terms of two superimposed $CHCl_3$ molecules, the density was eventually fitted by five anisotropic "atoms" with site occupation factors of 0.8 (Cl 41), 0.7 (Cl 42 and Cl 43) and 0.4 (Cl 44 and Cl 45).

Table 6. *Summary of experimental conditions*

		1	**2**
chemical formula		$C_{31}H_{38}N_4O_4 \cdot CHCl_3$	$C_{28}H_{34}N_4O_2 \cdot CHCl_3$
crystal size [mm]		$.05 \times .05 \times .2$	$.05 \times .2 \times .3$
temperature [K] (cold stream)		97 ± 1	96 ± 1
space group		$P\bar{1}$	$P2_1/c$
cell dimensions	a [A]	10.084 (3)	12.802 (1)
	b [A]	12.781 (2)	10.286 (2)
	c [A]	13.671 (5)	23.082 (8)
	α [°]	70.84 (1)	90
	β [°]	81.27 (1)	104.71 (1)
	γ [°]	83.86 (1)	90
	V [A^3]	1 642.0	2 939.8
number of molecules per unit cell		2	4
calculated density [$g\,cm^{-3}$]		1.315	1.306
number and θ-range [°] of reflections		20	33
used to refine cell constants		$7 \leqslant 2\theta \leqslant 16$	$17 \leqslant 2\theta \leqslant 21$
limits for data collection [°]		$0 \leqslant 2\theta \leqslant 50$	$0 \leqslant 2\theta \leqslant 50$
		$-11 \leqslant h \leqslant 11$	$0 \leqslant h \leqslant 15$
		$-15 \leqslant k \leqslant 15$	$0 \leqslant k \leqslant 12$
		$0 \leqslant l \leqslant 16$	$-27 \leqslant l \leqslant 27$
scan width [°] (ω/θ-scan)		1.5	1.2
number/frequency of standard refs.		2/100	2/100
max. variation of standard intensities		$\pm 4\%$	$\pm 3\%$
number of observed reflections		6 163	6 155
number of independent reflections		5 773	5 176
number of reflections with $\lvert F_o \rvert > 4\sigma(F_o)$		1 026	1 836
R/R_w-factors		0.117	0.056/0.047
number of parameters		368	483
number of observations (including distance constraints)		1 026	1 864
weighting system		unit weights	$1/\sigma^2(F_i)$
highest peak/lowest trough in final ΔF-Fourier synthesis [eA^{-3}]		0.6/−0.5	0.3/−0.4

The refinement of **2** was considerably less problematic: all non-hydrogen atoms were refined with anisotropic temperature factors, while hydrogens were refined with isotropic temperature factors. All C−H bonding distances involving sp^3-hybridized carbon atoms were constrained to 1.09 Å.

The computer programs used (some in locally modified versions) are summarized in Ref.[14].

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