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Crystal Structure and Conformation of 10-Aryl-bilatrienes-abc

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Summary. Crystal structure determinations of etiobiliverdin-IVγ (**1**) and of two *meso*-substituted arylbilatrienes-abc (the 2-imidazolylderivative **2** and the 4-nitrophenylderivative **3**) are reported. All three molecules have a *Z*, *Z*, *Z* configuration and occur in the crystal in an *all-syn* conformation, which results in a helical overall molecular shape. As a consequence of the steric repulsion between the aryl substituent and the two methyl groups on positions 8 and 12, the pitch and the curvature of the helix are larger in the two *meso*-substituted derivatives **2** and **3** compared to **1**. In each structure, the packing is dominated by the formation of centrosymmetric, S-shaped dimers via two hydrogen bonds between the pyrrolic H-atom and the carbonyl oxygen of ring A of two molecules related by the operation of an inversion center.

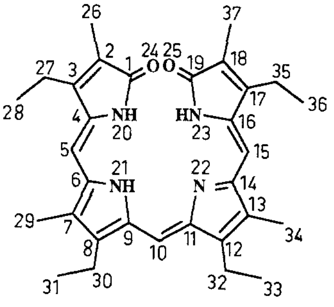
Keywords. Bile pigments; Linear tetrapyrroles; Bilatriene-abc; Crystal structure; Aryl-bilatriene-abc; Aetiobiliverdin-IVγ.

Kristallstruktur und Konformation von 10-Aryl-bilatrienen-abc

Zusammenfassung. Es wird über Kristallstrukturbestimmungen von Aetiobiliverdin-IVγ (**1**) sowie zweier *meso*-substituierter Arylbilatriene-abc (dem 2-Imidazolylderivat **2** und dem 4-Nitrophenylderivat **3**) berichtet. Alle drei Moleküle liegen im Kristall in einer *Z*, *Z*, *Z* Konfiguration vor und nehmen eine *all-syn*-Konformation ein, woraus sich eine helikale Molekülgestalt ergibt. Als Folge der sterischen Abstoßung zwischen dem Arylsubstituenten und den beiden Methylgruppen an den Positionen 8 und 12 sind die Ganghöhe und die Krümmung der Helix in den beiden *meso*-substituierten Derivaten **2** und **3** gegenüber **1** vergrößert. Die Kristallpackung wird in den drei Kristallstrukturen bestimmt durch die Ausbildung S-förmiger, zentrosymmetrischer Dimeren, die durch zwei intermolekulare Wasserstoffbrücken zwischen dem pyrrolischen Wasserstoffatom und dem Carbonylsauerstoff von Ring A zweier zentro-symmetrieäquivalenter Moleküle zusammengehalten werden.

Introduction

Linear tetrapyrroles of the 1,19-bilindione and 2,3-dihydrobilindione types have been studied as model compounds for the structural and functional aspects of animal metabolism and of biological pigment systems for photosynthesis and photomorphogenesis [1]. Several crystal structure determinations of 2,3-dihydro-1,19-bilindiones [2 – 5] and of 1,19-bilindiones [6 – 12] were reported in the past. In the case of the latter class of compounds it turned out that – with the exception of a 1-O-methylderivative [7] and of a 5-nitroderivative [8, 9] – disorder severely



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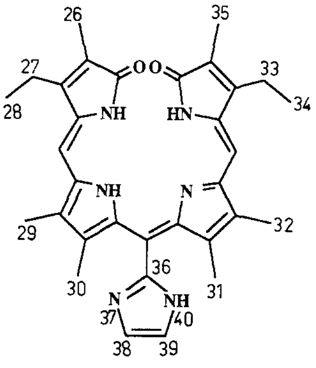

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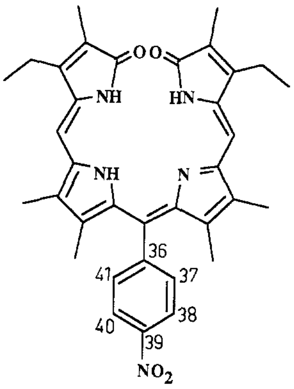

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limited the significance of the structural results. Often the disorder was due to the combination of an unsymmetrical substitution pattern and the formation of dimers in the crystal [11, 12]. However, the symmetrically substituted octaethyl-1,19-bilindione also showed disorder resulting from several conformations of the ethyl groups [6]. In addition to these small-molecule crystal structure determinations, several determinations of the crystal structures of natural pigments have been reported [13, 14].

In the present communication, we describe structural investigations on etiobiliverdin-IVγ (**1**) and two *meso*-substituted derivatives. Etiobiliverdin-IVγ is one of the most intensely studied model systems in the field of linear tetrapyrroles (for its synthesis see [15]), with a highly symmetrical substitution pattern. Formal demethylation in positions 8 and 12 and aryl substitution in position 10 lead to derivatives **2** and **3**. Extreme conformational variations were reported for the 2-imidazolylderivative **2** [16] and the 4-nitrophenylderivative **3** [17] in solution: while **3** assumes a helical conformation in most solvents, the conformation of **2** is strongly dependent on the solvent: in polar, protic solvents (such as methanol), it occurs in a helical, in apolar solvents (e.g. chloroform) in an extended conformation.

Results and Discussion

Due to a combination of circumstances (disorder, twinning, small crystal specimen size) none of the three structure determinations is very accurate. This is evident from the relatively high figures of merit and from the e.s.d.'s of the bonding distances (Table 1). Moreover, systematic errors due to crystal twinning occurred during the determination of reflection intensities for **2** (see Experimental).

Intramolecular Hydrogen Bonding and Tautomeric Form

Only in the crystal structure of **3** could all three hydrogen atoms attached to the pyrrolic nitrogens be determined experimentally from difference electron density maps. In each of the other two structures, one of these hydrogen atoms could not be observed and had to be inferred from the distribution of bondlengths (Table 3) and from the pattern of intra- and intermolecular hydrogen bonds; however, since

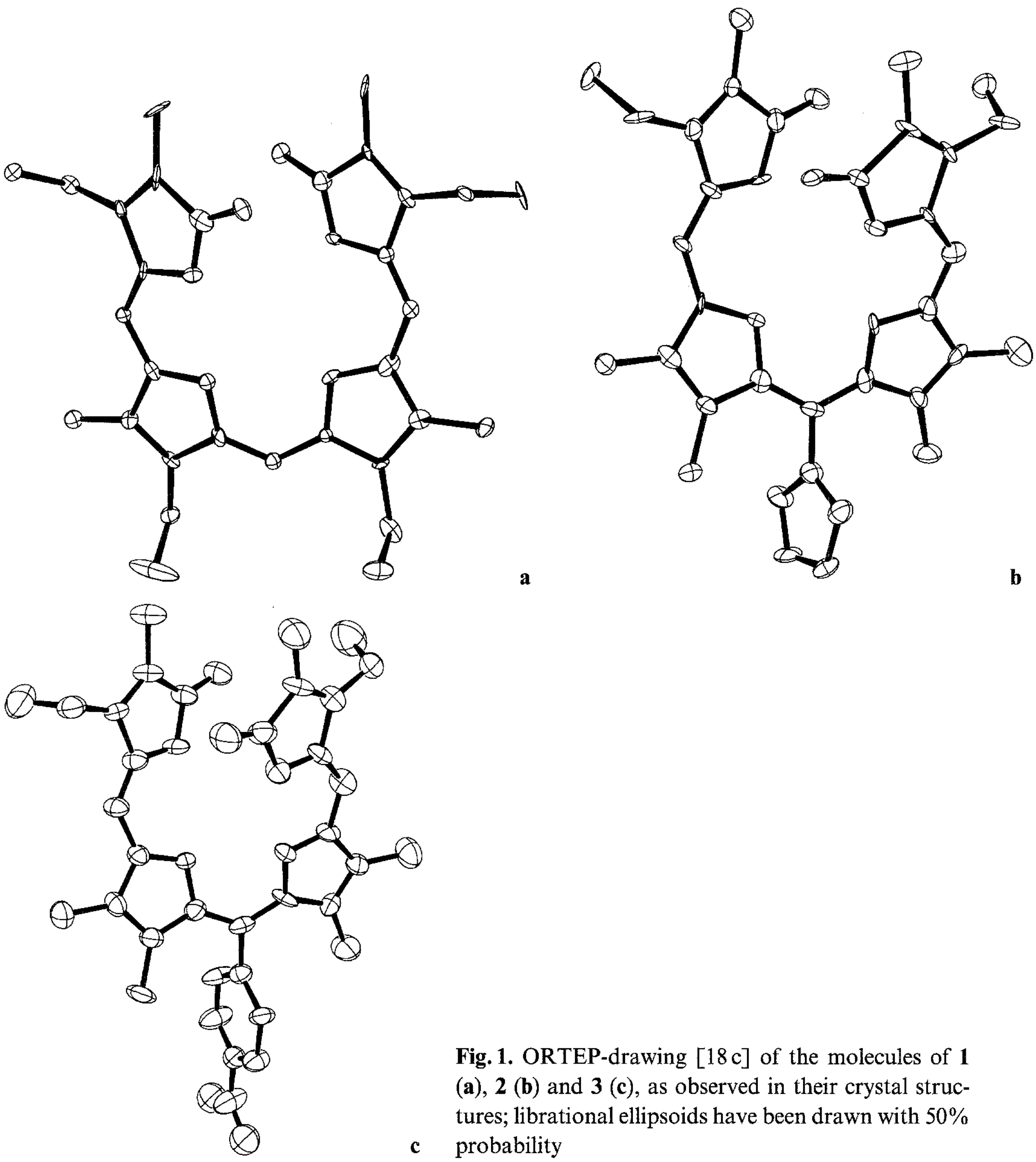

Fig. 1. ORTEP-drawing [18c] of the molecules of **1** (**a**), **2** (**b**) and **3** (**c**), as observed in their crystal structures; librational ellipsoids have been drawn with 50% probability

the tautomeric form manifests itself clearly in the distribution of the bonding distances of (formal) single and double bonds [2], the assignment of the "missing" pyrrolic protons and the verification of the observed ones was straightforward. The atom numbering has been consistently chosen such that the three pyrrolic protons are bonded to N 20, N 21, and N 23. In each of the three structures, the imine N-atom N 22 is observed within hydrogen bonding distance from the pyrrolic protons at the adjacent rings B and D (**1**: H 20...N 22, 3.53 Å, H 21...N 22, 2.24 Å, H 23...N 22, 2.15 Å; **2**: H 20...N 22, 3.39 Å, H 21...N 22, 2.13 Å, H 23...N 22, 2.07 Å; **3**: H 20...N 22, 3.28 Å, H 21...N 22, 2.07 Å, H 23...N 22, 2.14 Å), consistent with the helical overall conformation (see below).

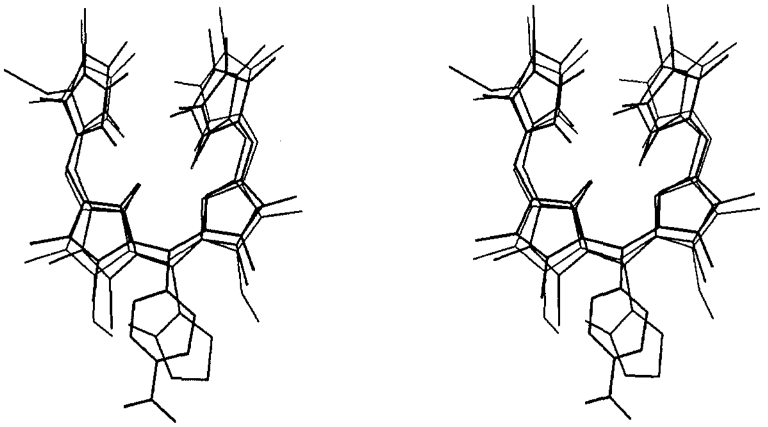

Fig. 2. Stereo-representation of a least-squares superposition of the molecules of **1**, **2**, and **3**, as observed in the crystal; the linewidth increases in the order **1**, **2**, **3**

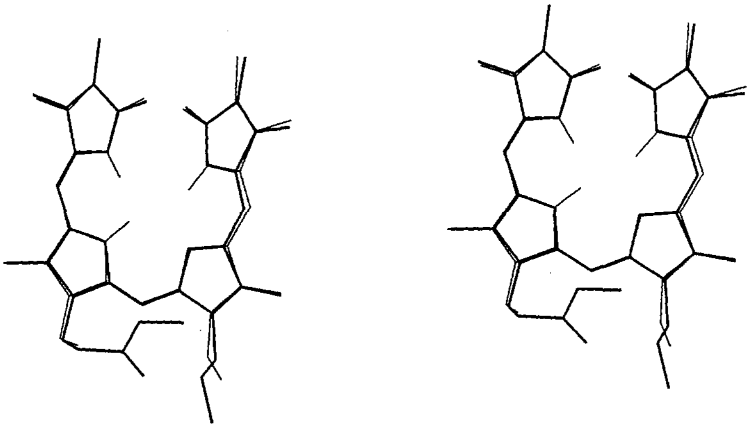

Fig. 3. Least-squares superposition of the asymmetric unit of the crystal structure of **1** with the crystal structure of biliverdin dimethyl ester [10]

Configuration and Conformation

As expected and as observed in solution in most solvents, the three compounds assume a *Z*, *Z*, *Z* configuration with *all-syn* conformation. This amounts to a helical molecular shape, as shown in Fig. 1 for the three molecules. The stereo-drawing of a least-squares superposition of the three molecules as observed in the crystal structures is shown in Fig. 2; the r. m. s. deviations of the 23 atoms of the linear tetrapyrrolic species (C 1 to C 19, N 20, N 21, N 22 and N 23) are 0.53 Å (superposition of **1** and **2**), 0.49 Å (**1** and **3**), and 0.44 Å (**2** and **3**). These deviations are large compared to the corresponding superposition of **1** with the crystal structure of biliverdin dimethyl ester [10] shown in Fig. 3 (r. m. s. deviation 0.11 Å).

Some of the conformational differences between **1**, **2**, and **3** are probably due to the steric repulsion between the aryl substituent on C 10 and the two substituents on position 8 and 12: the distance between the two methyl carbon atoms C 30 and

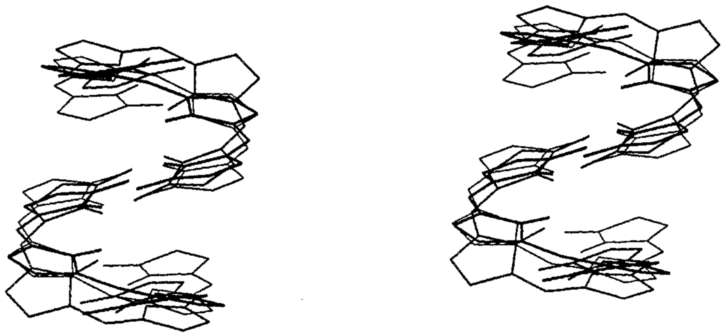

Fig. 4. Least-squares superposition of the centrosymmetric dimers, as observed in the crystal structures of **1**, **2**, and **3**. The superposition involved the atoms C1 to C19, N20, N21, N22, and N23 for both symmetry-equivalent molecules; the r. m. s. deviation of the superimposed atoms is 0.82 Å (superposition of **1** and **2**) and 0.76 Å (superposition of **1** and **3**)

C31 is 6.12 Å in **2** and 6.14 Å in **3**, whereas the corresponding distance between the two methylene carbon atoms C30 and C32 is only 5.55 Å in **1**. This steric interaction leads to an increase in the O24...O25 distance (3.25 Å in **1**, 4.31 Å in **2**, and 4.45 Å in **3**) reflecting two kinds of molecular distorsion: an increase in the helix pitch and an increase in the curvature of the helix, i.e. in the overlap between rings A and D (Fig. 2).

As predicted from a variety of spectroscopic and chemical arguments [17], the aryl substituent assumes a conformation intermediate between coplanar and perpendicular to the bilinchromophore (**2**: dihedral angle C9...C10...C36...N40, 65°; **3** dihedral angle C9...C10...C36...C41, 71°).

Intermolecular Hydrogen Bonds and Crystal Packing

In all three crystal structures the primary motive of molecular interactions is the formation of S-shaped dimers. The dimer formation is the result of two intermolecular H21...O24 hydrogen bonds, which link the two symmetry equivalent molecules across a center of symmetry (**1**: H21...O$24_{-x,-y,-z}$, 1.73 Å; **2**: H21...O$24_{-x,-y,-z}$, 1.79 Å; **3**: H21...O$24_{-x,-y,-z}$, 1.79 Å). A superposition of the so-formed dimers is shown in Fig. 4.

Experimental

X-ray experiments were performed on a locally modified STOE 4-circle diffractometer equipped with a NONIUS low temperature device. Graphite-monochromatized MoK_{α}-radiation ($\lambda = 0.71069$ Å) was used throughout. At an early stage of the diffractometer investigation of **2** it became evident that the crystal specimen under investigation was twinned. Since no other suitable crystal was available, we collected intensity data for the larger of the two twins, although some of the reflections could be indexed for both crystal lattices, i.e. the intensity data set suffers from a considerable systematic error. We made no attempt towards correcting this error.

Intensity data processing involved the usual L/P-correction, but no absorption correction. None of the three structures could be solved by straightforward application of direct methods: The structure of **1** was eventually solved with program MULTAN [18d], using a "random fragment" for the E-

Table 1. Experimental crystal data, data collection, and refinement parameters

Formula	$C_{31}H_{38}N_4O_2$	$C_{32}H_{36}N_6O_2.CH_3OH$	$C_{35}H_{37}N_5O_4.CHCl_3$
Formula weight	498.7	536.7+32.0	591.7+119.4
crysallized from	$CHCl_3$ / n-Hexane	MeOH / n-Hexane	$CHCl_3$ / n-Hexane
Crystal size [mm]	0.3x0.1x0.1	0.3x0.3x0.05	0.3x0.15x0.15
Temperature [K]	98 [1]	102 [1]	296 [2]
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
Z	2	2	2
Cell dimensions: a [Å]	9.672 [3]	11.016 [9]	11.232 [6]
b [Å]	10.856 [5]	11.201 [5]	12.441 [13]
c [Å]	13.645 [13]	15.440 [11]	14.251 [6]
α [°]	82.99 [1]	92.81 [4]	75.13 [5]
β [°]	77.54 [1]	109.83 [6]	70.47 [3]
γ [°]	80.32 [3]	116.76 [5]	88.63 [5]
V [$Å^3$]	1373.7 [9]	1553.5 [9]	1810.0 [9]
Nr./ϑ-range of Refs. used for cell refinement	16 / $5^\circ \le 2\vartheta \le 15^\circ$	40 / $7^\circ \le 2\vartheta \le 21^\circ$	21 / $7^\circ \le 2\vartheta \le 20^\circ$
Calc. density d_x [g/cm^3]	1.205	1.216	1.305
Data collection range	$3.0^\circ \le 2\vartheta \le 50^\circ$ $-11 \le h \le 11$ $-12 \le k \le 12$ $0 \le l \le 16$	$3.5^\circ \le 2\vartheta \le 45^\circ$ $-11 \le h \le 11$ $-12 \le k \le 12$ $0 \le l \le 16$	$3.5^\circ \le 2\vartheta \le 40^\circ$ $-10 \le h \le 10$ $-11 \le k \le 11$ $0 \le l \le 13$
Scan type / scan range	ω / 1.2°	ω/ϑ / 1.2°	ω/ϑ / 1.2°
Nr. total data recorded	14 314	4 346	3 851
Nr. unique data	4 849	4 024	3 477
Nr. observed data with $F > x\,\sigma(F)$ / x	1 483 / 6.0	2 372 / 4.0	1 918 / 4.0
Weighting scheme	$w=1/\sigma^2(\lvert F_o\rvert)$	$w=1/\sigma^2(\lvert F_o\rvert)$	$w=1/\sigma^2(\lvert F_o\rvert)$
No. obs./no. parameters	1 490 / 470	2 380 / 420	1 960 / 488
$R=\Sigma\lVert F_o\rvert-\lvert F_c\rVert/\Sigma\lvert F_o\rvert$ / R_w	0.077 / 0.056	0.135 / 0.136	0.094 / 0.094
e.s.d. of a C-C bondlength	0.013 Å	0.020 Å	0.018 Å
Highest peak in final ΔF-map [$eÅ^{-3}$]	0.13	0.7	0.25
anisotropic non-H atoms	C-1...C-37	C-1...C-40	C-1...C-41
isotropic non-H atoms		O-41 , C-42	N-42...Cl-3B
No. H-atoms obs. / calc.	35 / 3	5 / 34	5 / 32
acidic H-atoms observed	H-21 , H-23	H-20, H-23 , H-40	H-20...H-23
acidic H-atoms calculated	H-20	H-21	

normalization. Solution of the structures of **2** and **3** was only possible with Patterson-search techniques (PATSEE, [18 f]), using part of the crystal structure of **1** as input. Least-squares refinement (Program SHELX 76, [18 b]) involved the determination of anisotropic atomic displacement parameters (a.d.p.'s) for all non-hydrogen atoms with the exception of disordered atoms and atoms from solvent molecules. Hydrogen atoms whose position could be determined from a difference Fourier synthesis were refined with isotropic a.d.p.'s and a restraint on the corresponding C-H or N-H bondlength. The positions of most of the remaining H atoms were computed on the basis of stereochemical plausibility; for each of these H atoms, only an isotropic a.d.p. was refined. Experimental parameters and crystallographic results are summarized in Table 1.

Table 2. Atomic coordinates ($\times 10^4$) and displacement coefficients ($\times 10^4$, U-values in Å^2) for **1** (a), **2** (b) and **3** (c). e.s.d.'s in parentheses. The anisotropic temperature factor has the form $T = \exp[-2\pi^2(h^2a^{*2}U_{11} + \ldots + 2hka^*b^*U_{12} + \ldots)]$, the isotropic temperature factor has the form $T = \exp(-8\pi^2 U_{11} \sin^2\Theta/\lambda^2)$. Equivalent isotropic U-values were computed as one third of the trace of the orthogonalized U_{ij}-tensor. H atoms bonded to pyrrolic or imidazole N atoms are given at their calculated positions

a

	X/a	Y/b	Z/c	U_{iso}
C-1	-1874 *(9)*	472 *(8)*	890 *(7)*	216 *(64)*
C-2	-3357 *(9)*	1047 *(8)*	1375 *(7)*	137 *(60)*
C-3	-4080 *(9)*	1364 *(8)*	614 *(7)*	142 *(61)*
C-4	-3146 *(8)*	980 *(8)*	-353 *(7)*	150 *(61)*
C-5	-3508 *(9)*	1076 *(9)*	-1252 *(7)*	144 *(60)*
C-6	-2767 *(9)*	547 *(9)*	-2165 *(7)*	213 *(67)*
C-7	-3156 *(9)*	788 *(8)*	-3112 *(7)*	173 *(63)*
C-8	-2217 *(9)*	-13 *(8)*	-3779 *(6)*	135 *(60)*
C-9	-1266 *(8)*	-774 *(7)*	-3213 *(6)*	109 *(54)*
C-10	-123 *(10)*	-1753 *(8)*	-3549 *(7)*	161 *(61)*
C-11	645 *(9)*	-2615 *(8)*	-2957 *(7)*	177 *(59)*
C-12	1928 *(9)*	-3456 *(8)*	-3337 *(7)*	131 *(58)*
C-13	2421 *(9)*	-4015 *(8)*	-2512 *(7)*	165 *(59)*
C-14	1475 *(9)*	-3481 *(8)*	-1637 *(7)*	167 *(63)*
C-15	1594 *(9)*	-3764 *(8)*	-575 *(7)*	131 *(62)*
C-16	616 *(9)*	-3367 *(8)*	215 *(7)*	132 *(58)*
C-17	747 *(9)*	-3467 *(8)*	1275 *(7)*	164 *(64)*
C-18	-519 *(9)*	-2901 *(8)*	1813 *(7)*	223 *(65)*
C-19	-1536 *(10)*	-2526 *(8)*	1113 *(7)*	259 *(68)*
N-20	-1796 *(7)*	450 *(6)*	-112 *(5)*	172 *(47)*
N-21	-1599 *(7)*	-416 *(6)*	-2251 *(5)*	128 *(45)*
N-22	367 *(6)*	-2658 *(6)*	-1910 *(5)*	153 *(45)*
N-23	-767 *(7)*	-2758 *(7)*	164 *(5)*	179 *(50)*
O-24	-862 *(5)*	101 *(5)*	1353 *(4)*	189 *(39)*
O-25	-2812 *(6)*	-2050 *(5)*	1322 *(4)*	198 *(40)*
C-26	-3805 *(10)*	1151 *(8)*	2475 *(7)*	189 *(59)*
C-27	-5635 *(9)*	1980 *(8)*	697 *(7)*	168 *(59)*
C-28	-5724 *(10)*	3382 *(8)*	245 *(8)*	232 *(65)*
C-29	-4359 *(11)*	1772 *(9)*	-3361 *(7)*	211 *(65)*
C-30	-2296 *(10)*	-221 *(8)*	-4849 *(8)*	238 *(64)*
C-31	-3187 *(11)*	-1206 *(10)*	-4909 *(8)*	288 *(73)*
C-32	2552 *(10)*	-3628 *(8)*	-4434 *(7)*	207 *(61)*
C-33	1930 *(17)*	-4558 *(12)*	-4891 *(9)*	808 *(128)*
C-34	3789 *(9)*	-4916 *(8)*	-2459 *(8)*	198 *(62)*
C-35	2067 *(9)*	-4024 *(8)*	1700 *(7)*	174 *(59)*
C-36	1862 *(9)*	-5287 *(7)*	2329 *(7)*	187 *(60)*
C-37	-937 *(11)*	-2629 *(11)*	2902 *(7)*	304 *(74)*
H-20	-860	88	-643	
H-21	-1046	-815	-1652	
H-23	-1172	-2506	-523	

b

	X/a	Y/b	Z/c	U_{iso}
C-1	-489 *(14)*	981 *(13)*	9002 *(9)*	273 *(108)*
C-2	-1113 *(13)*	1704 *(13)*	8349 *(8)*	226 *(99)*
C-3	-1398 *(13)*	2476 *(13)*	8867 *(9)*	246 *(104)*
C-4	-983 *(13)*	2289 *(12)*	9850 *(8)*	202 *(97)*
C-5	-1099 *(13)*	2924 *(13)*	10581 *(8)*	205 *(101)*
C-6	-480 *(13)*	3036 *(12)*	11571 *(8)*	201 *(97)*
C-7	-625 *(14)*	3732 *(13)*	12273 *(9)*	269 *(110)*
C-8	339 *(14)*	3770 *(14)*	13178 *(9)*	284 *(110)*
C-9	1052 *(14)*	3049 *(12)*	13027 *(9)*	269 *(104)*
C-10	2189 *(14)*	2855 *(13)*	13693 *(8)*	243 *(104)*
C-11	3073 *(13)*	2451 *(13)*	13419 *(9)*	249 *(99)*
C-12	4158 *(14)*	2065 *(13)*	13945 *(9)*	245 *(106)*
C-13	4752 *(13)*	1791 *(12)*	13368 *(8)*	235 *(98)*
C-14	4033 *(14)*	2103 *(13)*	12460 *(10)*	297 *(109)*
C-15	4352 *(14)*	2014 *(13)*	11637 *(9)*	261 *(105)*
C-16	3907 *(13)*	2605 *(12)*	10920 *(8)*	177 *(96)*
C-17	4144 *(13)*	2655 *(12)*	10010 *(8)*	205 *(104)*
C-18	3550 *(15)*	3340 *(13)*	9526 *(9)*	276 *(108)*
C-19	2915 *(14)*	3844 *(13)*	10082 *(8)*	255 *(106)*
N-20	-459 *(11)*	1373 *(11)*	9868 *(6)*	257 *(88)*
N-21	524 *(11)*	2591 *(10)*	12051 *(7)*	221 *(82)*
N-22	3074 *(10)*	2482 *(10)*	12504 *(7)*	217 *(80)*
N-23	3204 *(11)*	3374 *(10)*	10905 *(7)*	233 *(83)*
O-24	-76 *(10)*	166 *(8)*	8799 *(6)*	294 *(73)*
O-25	2353 *(9)*	4570 *(9)*	9910 *(5)*	275 *(72)*
C-26	-1189 *(16)*	1570 *(15)*	7366 *(9)*	334 *(121)*
C-27	-2009 *(15)*	3411 *(13)*	8514 *(8)*	287 *(108)*
C-28	-3610 *(14)*	2608 *(16)*	7752 *(10)*	422 *(119)*
C-29	-1561 *(15)*	4434 *(14)*	12125 *(9)*	309 *(118)*
C-30	592 *(17)*	4537 *(17)*	14135 *(9)*	455 *(137)*
C-31	4479 *(19)*	1835 *(17)*	14973 *(9)*	452 *(150)*
C-32	5948 *(17)*	1406 *(15)*	13554 *(11)*	420 *(137)*
C-33	4905 *(16)*	1924 *(13)*	9760 *(9)*	311 *(116)*
C-34	3703 *(15)*	446 *(14)*	9156 *(9)*	371 *(117)*
C-35	3388 *(15)*	3608 *(13)*	8536 *(8)*	306 *(109)*
C-36	2571 *(14)*	3238 *(14)*	14717 *(9)*	283 *(108)*
N-37	3850 *(12)*	4281 *(11)*	15304 *(8)*	349 *(99)*
C-38	3769 *(15)*	4374 *(13)*	16200 *(9)*	290 *(111)*
C-39	2362 *(16)*	3322 *(15)*	16066 *(9)*	389 *(129)*
N-40	1647 *(13)*	2627 *(12)*	15141 *(7)*	341 *(99)*
O-41	1251 *(13)*	9671 *(12)*	5567 *(8)*	735 *(35)*
C-42	1768 *(20)*	10089 *(18)*	6570 *(12)*	645 *(50)*
H-20	-75	1013	10485	
H-21	837	1981	11708	
H-23	2913	3585	11473	
H-40	540	1746	14808	

Disorder was observed in the structures of **3**, affecting the nitro group and the solvent chloroform molecule: the four peaks observed for the two oxygen atoms of the nitro group were accounted for by four oxygen atoms, two of them with population p and the other two with 1 − p. p was refined together with a common isotropic a.d.p. and positional parameters for all four partial O atoms subject to a distance restraint for the four N-O bondlengths (1.22 Å). p converged to 0.83 (1). Similarly, six electron density maxima were observed for the three chlorine atoms of the chloroform solvent molecule; a partial Cl-atom was refined at each of these peaks, with an individual isotropic a.d.p.

Table 2 (continued)

c

	X/a	Y/b	Z/c	U_{iso}
C-1	1673 *(11)*	-435 *(10)*	9155 *(9)*	521 *(101)*
C-2	2970 *(12)*	-511 *(10)*	8522 *(9)*	544 *(103)*
C-3	3738 *(11)*	165 *(9)*	8718 *(8)*	479 *(91)*
C-4	2946 *(11)*	653 *(10)*	9527 *(9)*	489 *(101)*
C-5	3351 *(11)*	1318 *(10)*	9971 *(9)*	485 *(94)*
C-6	2660 *(12)*	1650 *(9)*	10887 *(10)*	466 *(98)*
C-7	3054 *(10)*	2457 *(10)*	11284 *(10)*	515 *(98)*
C-8	2103 *(12)*	2455 *(10)*	12213 *(9)*	546 *(99)*
C-9	1148 *(11)*	1647 *(10)*	12389 *(10)*	492 *(97)*
C-10	17 *(12)*	1248 *(10)*	13225 *(9)*	475 *(99)*
C-11	-698 *(12)*	269 *(10)*	13442 *(10)*	509 *(104)*
C-12	-1954 *(11)*	-133 *(10)*	14147 *(8)*	476 *(92)*
C-13	-2213 *(11)*	-1078 *(10)*	13947 *(9)*	513 *(96)*
C-14	-1119 *(10)*	-1239 *(8)*	13127 *(9)*	463 *(92)*
C-15	-995 *(11)*	-2144 *(10)*	12652 *(10)*	553 *(101)*
C-16	97 *(11)*	-2422 *(8)*	12038 *(9)*	472 *(94)*
C-17	337 *(13)*	-3358 *(10)*	11511 *(10)*	589 *(104)*
C-18	1597 *(13)*	-3318 *(9)*	11014 *(10)*	555 *(105)*
C-19	2255 *(11)*	-2406 *(10)*	11192 *(9)*	621 *(102)*
N-20	1687 *(10)*	259 *(7)*	9756 *(7)*	524 *(85)*
N-21	1509 *(9)*	1197 *(7)*	11558 *(7)*	449 *(75)*
N-22	-211 *(8)*	-454 *(6)*	12842 *(7)*	479 *(67)*
N-23	1287 *(8)*	-1896 *(7)*	11794 *(7)*	552 *(74)*
O-24	692 *(7)*	-930 *(6)*	9195 *(6)*	667 *(66)*
O-25	3355 *(7)*	-2126 *(7)*	10890 *(7)*	851 *(73)*
C-26	3318 *(14)*	-1276 *(12)*	7800 *(11)*	816 *(139)*
C-27	5160 *(11)*	328 *(11)*	8262 *(10)*	656 *(110)*
C-28	5585 *(16)*	1352 *(15)*	7353 *(13)*	1138 *(170)*
C-29	4305 *(12)*	3125 *(12)*	10773 *(12)*	800 *(126)*
C-30	2231 *(13)*	3188 *(14)*	12893 *(11)*	953 *(144)*
C-31	-2817 *(14)*	363 *(13)*	14980 *(13)*	960 *(146)*
C-32	-3393 *(11)*	-1884 *(11)*	14494 *(13)*	841 *(131)*
C-33	-674 *(11)*	-4077 *(9)*	11494 *(10)*	622 *(100)*
C-34	-1157 *(18)*	-3569 *(14)*	10623 *(14)*	1205 *(190)*
C-35	2309 *(13)*	-4059 *(12)*	10381 *(13)*	878 *(134)*
C-36	-481 *(10)*	2075 *(9)*	13883 *(9)*	462 *(90)*
C-37	-417 *(11)*	1849 *(10)*	14867 *(9)*	567 *(100)*
C-38	-815 *(12)*	2700 *(10)*	15413 *(10)*	635 *(105)*
C-39	-1280 *(11)*	3619 *(10)*	14987 *(10)*	534 *(100)*
C-40	-1379 *(13)*	3825 *(11)*	14056 *(11)*	844 *(131)*
C-41	-998 *(12)*	3062 *(11)*	13493 *(9)*	721 *(117)*
N-42	-1691 *(14)*	4460 *(11)*	15580 *(9)*	1011 *(122)*
O-43A[a]	-1509 *(14)*	4282 *(11)*	16419 *(10)*	951 *(30)*
O-43B[a]	-2379 *(50)*	4053 *(43)*	16477 *(21)*	951 *(30)*
O-44A[a]	-2113 *(11)*	5285 *(10)*	15197 *(10)*	951 *(30)*
O-44B[a]	-847 *(44)*	4695 *(50)*	15877 *(52)*	951 *(30)*
C-LM	4963 *(14)*	5098 *(13)*	6886 *(12)*	956 *(46)*
Cl-1A[a]	4187 *(14)*	4280 *(6)*	6372 *(6)*	1056 *(47)*
Cl-1B[a]	4857 *(68)*	4122 *(29)*	6269 *(25)*	1477 *(181)*
Cl-2A[a]	4143 *(9)*	6314 *(11)*	6867 *(17)*	1180 *(50)*
Cl-2B[a]	3973 *(15)*	6018 *(17)*	7418 *(26)*	1053 *(87)*
Cl-3A[a]	4712 *(23)*	4402 *(12)*	8153 *(14)*	1129 *(80)*
Cl-3B[a]	5389 *(19)*	4205 *(9)*	7853 *(11)*	1131 *(64)*
H-20	864	472	10317	
H-21	952	570	11454	
H-23	1440	-1177	12043	

[a] Atom with partial occupancy, for exact value of s. o. f. see experimental section

and individual population parameter for each partial Cl atom; they converged to the following values: Cl 1 A, 0.70; Cl 1 B, 0.21; Cl 2 A, 0.57; Cl 2 B, 0.39; Cl 3 A, 0.38; Cl 3 B, 0.49. Atomic coordinates are given in Table 2, computer programs used are listed in Ref. [18].

Table 3. Bond lengths in the crystal structures of **1**, **2**, and **3**. The standard deviations (of a typical C-C bond) are approximately 0.013 Å for **1**, 0.020 Å for **2**, and 0.018 Å for **3**

C1-C2	1.51	1.50	1.45
C2-C3	1.35	1.35	1.36
C3-C4	1.49	1.49	1.46
C4-C5	1.33	1.38	1.33
C5-C6	1.43	1.42	1.44
C6-C7	1.41	1.40	1.42
C7-C8	1.41	1.42	1.40
C8-C9	1.42	1.41	1.40
C9-C10	1.44	1.44	1.41
C10-C11	1.39	1.41	1.38
C11-C12	1.45	1.45	1.44
C12-C13	1.35	1.37	1.34
C13-C14	1.46	1.50	1.44
C14-C15	1.47	1.44	1.44
C15-C16	1.33	1.38	1.34
C16-C17	1.47	1.51	1.51
C17-C18	1.37	1.32	1.35
C18-C19	1.49	1.50	1.49
C1-N20	1.36	1.37	1.37
C4-N20	1.43	1.38	1.41
C6-N21	1.40	1.41	1.35
C9-N21	1.37	1.39	1.37
C11-N22	1.39	1.42	1.38
C14-N22	1.36	1.32	1.31
C16-N23	1.40	1.39	1.40
C19-N23	1.38	1.39	1.39
C1-O24	1.26	1.26	1.25
C19-O25	1.24	1.22	1.19

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