Monoclinic
$P2_1/c$
$a = 10.959$ (1) Å
$b = 12.963$ (1) Å
$c = 7.9905$ (8) Å
$\beta = 106.081$ (9)°
$V = 1090.7$ (2) Å^3
$Z = 4$
$D_x = 1.390$ Mg m^{-3}
D_m not measured

Cell parameters from 39 reflections
$\theta = 5.38$–$12.49°$
$\mu = 0.098$ mm^{-1}
$T = 293$ (2) K
Needle
0.50 × 0.24 × 0.18 mm
Colourless

Data collection

Siemens *P*4 diffractometer
$\theta/2\theta$ scans
Absorption correction: none
3279 measured reflections
2499 independent reflections
1257 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.025$

$\theta_{\rm max} = 27.50°$
$h = -14 \rightarrow 13$
$k = -16 \rightarrow 1$
$l = -1 \rightarrow 10$
3 standard reflections every 97 reflections intensity decay: <3%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.040$
$wR(F^2) = 0.105$
$S = 0.828$
2499 reflections
203 parameters
All H atoms refined
$w = 1/[\sigma^2(F_o^2) + (0.0484P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$

$\Delta\rho_{\rm max} = 0.178$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.136$ e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0131 (17)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 2. *Intermolecular interactions (Å, °) for (II)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C3—H3···O11$^{\rm i}$	0.94 (2)	2.64 (2)	3.495 (3)	152 (1)
C6—H6···O17$^{\rm ii}$	1.01 (2)	2.59 (2)	3.295 (2)	127 (1)

Symmetry codes: (i) $2 - x, 1 - y, -z$; (ii) $1 - x, -y, -z$.

Table 3. *Selected geometric parameters (Å, °) for (I) and (II)*

	(I)	(II)
C3—C4	1.337 (2)	1.338 (2)
C7—C12	1.491 (2)	1.509 (2)
C12—C13	1.459 (3)	1.490 (3)
C13—C14	1.324 (3)	1.451 (3)
C14—C15	1.474 (2)	1.493 (2)
C8—C15	1.493 (2)	1.503 (2)
C13—O17	–	1.448 (2)
C14—O17	–	1.443 (2)
C3—C2—O11	126.9 (2)	127.0 (2)
O1—C2—O11	115.7 (2)	116.2 (2)
O1—C9—C8	115.2 (1)	114.7 (1)
C4—C10—C5	124.6 (2)	124.7 (2)
C13—O17—C14	–	60.3 (1)

Data collection, cell refinement and data reduction: *XSCANS* (Siemens, 1994). Structure solution and molecular graphics: *SHELXTL/PC* (Sheldrick, 1990). Structure refinement: *SHELXL*93 (Sheldrick, 1993). Geometrical calculations: *PARST* (Nardelli, 1983*b*).

The authors would like to thank the Malaysian Government and the Universiti Sains Malaysia for research grant R&D No. 190-9609-2801. KC thanks the Universiti Sains Malaysia for a Visiting Postdoctoral Fellowship.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: CF1186). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1998). C**54**, 544–547

Two Dyotropomers Resulting from Irreversible Thermal ($4\sigma + 2\pi$) 2H Group Transfer

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(*Received 30 July 1997; accepted 12 November 1997*)

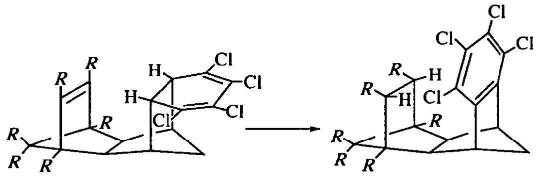
Abstract

The structures of two compounds, (1D) (*endo*-*endo*-1,5,6,7,8,12,13,14,15,15-decachloropentacyclo[10.2.1.1^{3,10}.0^{2,11}.0^{4,9}]hexadeca-4(9),5,7-triene, $C_{16}H_8Cl_{10}$) and (2D) (13,14-benzo-3,4,5,6-tetrachlorotetracyclo[6.4.2.2^{9,12}.0^{2,7}]hexadeca-2(7),3,5-triene, $C_{20}H_{16}Cl_4$), are reported. Both compounds are products of an irre-

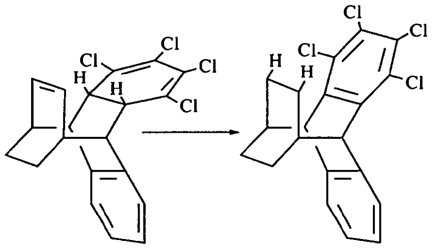
versible dyotropic rearrangement where two H atoms are transferred intramolecularly onto a proximate π bond. These compounds are two members of several different series of compounds being studied with the aim of understanding the factors affecting the rate of this type of 2H group-shift isomerization which can vary enormously with changes in the substitution pattern at, or near, the reaction zone. The atom-numbering system used for compounds of series (I) is that of Mackenzie *et al.* [*Tetrahedron* (1987), **43**, 5981–5993]. [The systematic name of (1D) using IUPAC nomenclature is *endo-endo*-3,4,5,6,10,11,12,13,16,16-decachloropentacyclo[6.6.1.1^{3,6}.0^{2,7}.0^{9,14}]hexadeca-9(14),10,12-triene.]

Comment

The two structures reported here are products of irreversible dyotropic rearrangements, (I) and (II), involving the intramolecular group transfer of two H atoms. The first series of compounds studied, (I), showed a huge variation in the rate of rearrangement depending on the *R* substituents (Mackenzie *et al.*, 1993, and references therein). For example, the replacement of R^{1-6} = H by R^{1-6} = Cl results in a reduction of the unimolecular rate constant, k_1, by a factor of 2×10^5 at 409 K (Mackenzie *et al.*, 1987).



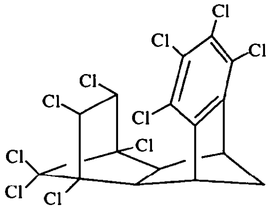
(I)



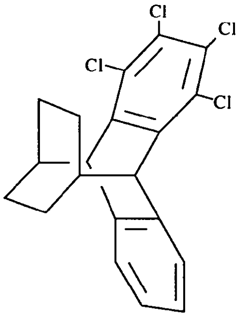
(II)

This observation prompted the synthesis and study of a series of related compounds which have a variety of substituent patterns (*R* = OMe, OEt, Cl, H), with the aim of investigating the factors affecting kinetic behaviour in dyotropy. These compounds provide suitable model systems for investigating such effects, since they rearrange cleanly with no side reactions, at conveniently measurable rates and have unique chromophores for UV absorption spectroscopic measurements. It has also proved possible to obtain good quality crystals of many of these compounds suitable for both X-ray and neutron studies, thus allowing the relationship between the structure and reactivity of these compounds to be explored (Mackenzie *et al.*, 1993; Wilson 1995).

The rearrangement is unambiguously seen to have occurred in (1D), an example from the first series, (I), where R^{1-6} = Cl. The two H atoms have transferred from positions C4 and C9 of the starting isomer to positions H13 and H14 in (1D). Other structural changes have also occurred with the rearrangement. For example, the six-membered ring C4–C9 has become aromatic in character, as indicated by the bond lengths and angles. This aromatization is thought to provide much of the driving energy for the rearrangement, although it is not a prerequisite for such reactions (Hagenbuch *et al.*, 1981; Geich *et al.*, 1992). Additionally, the geometry around the C13—C14 bridgehead is consistent with the expected sp^3 hybridization and a C—C single bond [1.564 (5) Å], compared with the starting-isomer geometry which is consistent with sp^2 hybridization and a C=C double bond [1.341 (2) Å], as determined from neutron-diffraction data measured at 15 K (Wilson, 1995).



(1D)



(2D)

Compound (2D) is an example from a more recent series of compounds, (II), also found to undergo analogous dyotropic rearrangement (Mackenzie *et al.*, 1996). Again, structural changes accompanying the rearrangement may be observed, *e.g.* the transfer of the H atoms from C2 and C7 in the starting isomer (Mackenzie *et al.*, 1996) to the H10 and H11 positions in this compound and the comparable aromatization of the six-membered ring containing atoms C2–C7.

In part, this second series of compounds was synthesized in order to introduce a more flexible framework into the structure and thus explore its effect on the rate of rearrangement. In general, all the compounds of series (I) have a very rigid and almost constant carbon skeleton. However, a considerable amount of discussion has been devoted to the relatively small differences between compounds of a given series, in particular, the role played by the proximity of the H atoms to the π-receptor element. Work on a related series of sesquinobornenes (Paquette *et al.*, 1990) suggested a correlation between the cross-cavity separations (*i.e.* between the transferring 2H group and the receptor element) as determined from room temperature X-ray studies and the rate of rearrangement. Indeed, in their earlier work, a rate spread of 10^4 s^{-1} was attributed to result from a change in this separation in the order of 0.1 Å, although subsequent work on other related systems indicated that the situation is more complex (Paquette *et al.*, 1991; O'Doherty *et al.*, 1994). Such a relationship has not been observed in the present compounds, neither in the X-ray studies carried out to date nor using the more accurately determined H-atom positions from low-temperature neutron data (Mackenzie *et al.*, 1993; Wilson, 1995). Interestingly, the cross-cavity separations C2···C11 and C7···C10 of 2.814 (4) and 2.813 (4) Å, respectively, in (2D) are very significantly shorter than the 3.05–3.10 Å range typical of the compounds of series (I). However, the rate of rearrangement is considerably smaller relative to series (I) compounds, with the rate ratio $k_1(1)$:$k_1(2)$ of 1.75 × 10^3 at 423 K, suggesting that other factors than proximity modulate reactivity in these rearrangements to a considerable extent. Further work is in progress to investigate the factors responsible.

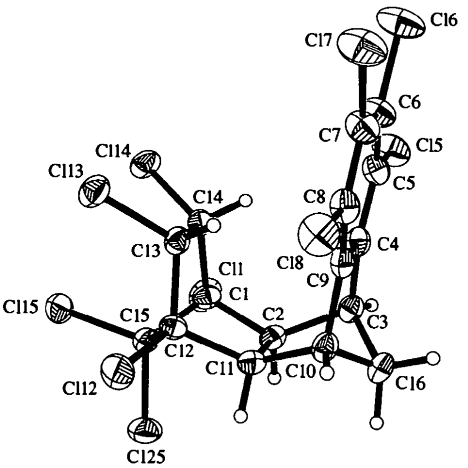


Fig. 1. The molecular structure of (1D) with 30% probability displacement ellipsoids.

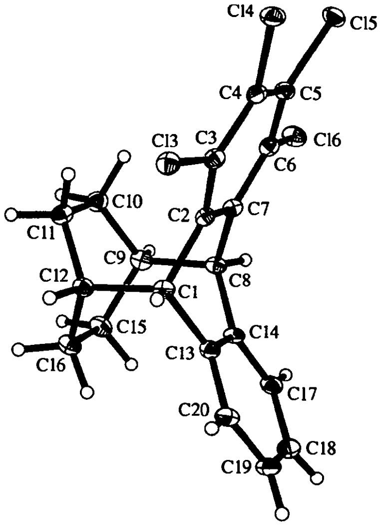


Fig. 2. The molecular structure of (2D) with 30% probability displacement ellipsoids.

Experimental

The title compounds were synthesized as described previously (Mackenzie *et al.*, 1993, 1996).

Compound (1D)

Crystal data

$C_{16}H_8Cl_{10}$
M_r = 554.72
Monoclinic
$C2/c$
a = 13.911 (3) Å
b = 10.357 (2) Å
c = 28.782 (6) Å
β = 102.87 (2)°
V = 4042.4 (14) Å^3
Z = 8
D_x = 1.823 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 10–15°
μ = 1.379 mm^{-1}
T = 293 (2) K
Plate
0.9 × 0.5 × 0.4 mm
Colourless

Data collection

Rigaku AFC-6*S* four-circle diffractometer
Profile recorded from ω scans
Absorption correction: empirical *via* ψ scans (*TEXSAN*; Molecular Structure Corporation, 1992)
T_{min} = 0.460, T_{max} = 0.576
4830 measured reflections

4642 independent reflections
2605 reflections with $I > 2\sigma(I)$
R_{int} = 0.032
θ_{max} = 27.5°
h = 0 → 18
k = 0 → 13
l = −37 → 36
3 standard reflections every 150 reflections intensity decay: 1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.046
$wR(F^2)$ = 0.074
S = 1.304
3896 reflections
268 parameters
All H atoms refined
$w = 1/[\sigma^2(F_o^2) + (0.005P)^2 + 1.0P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max}$ = −0.063
$\Delta\rho_{max}$ = 0.459 e Å^{-3}
$\Delta\rho_{min}$ = −0.395 e Å^{-3}
Extinction correction: *SHELXTL*
Extinction coefficient: 0.00099 (4)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °) for (1D)*

C4—C9	1.393 (4)	C13—C14	1.564 (5)
C12—C13—C14	103.2 (3)	C1—C14—C13	102.9 (3)

Compound (2D)

Crystal data

$C_{20}H_{16}Cl_4$
M_r = 398.13

Mo $K\alpha$ radiation
λ = 0.71073 Å

Triclinic
$P\bar{1}$
$a = 7.0543\ (7)$ Å
$b = 8.8125\ (9)$ Å
$c = 15.016\ (1)$ Å
$\alpha = 72.980\ (3)°$
$\beta = 77.562\ (3)°$
$\gamma = 69.707\ (3)°$
$V = 830.4\ (1)$ Å^3
$Z = 2$
$D_x = 1.592$ Mg m^{-3}
D_m not measured

Cell parameters from 510 reflections
$\theta = 7.0$–$24.1°$
$\mu = 0.711$ mm^{-1}
$T = 150\ (2)$ K
Rectangular
0.50 × 0.42 × 0.16 mm
Colourless

Data collection

Siemens SMART CCD diffractometer
ω rotation scans with narrow frames
Absorption correction: empirical *via* ψ scans (*SHELXTL*; Sheldrick, 1994)
$T_{\min} = 0.65$, $T_{\max} = 0.89$

3487 measured reflections
2560 independent reflections
2429 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.032$
$\theta_{\max} = 25.14°$
$h = -8 \rightarrow 7$
$k = -10 \rightarrow 7$
$l = -17 \rightarrow 17$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.039$
$wR(F^2) = 0.099$
$S = 1.118$
2554 reflections
266 parameters
Only coordinates of H atoms refined
$w = 1/[\sigma^2(F_o^2) + (0.0414P)^2 + 1.0763P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.295$ e Å^{-3}
$\Delta\rho_{\min} = -0.390$ e Å^{-3}
Extinction correction: *SHELXL*
Extinction coefficient: 0.072 (5)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 2. *Selected bond lengths (Å) for (2D)*

C2—C7	1.395 (3)	C12—C11	1.530 (4)

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1991) for (1D); *SMART* (Siemens, 1995) for (2D). Cell refinement: *TEXSAN* (Molecular Structure Corporation, 1992) for (1D); *SMART* for (2D). Data reduction: *TEXSAN* for (1D); *SAINT* (Siemens, 1995) for (2D). For both compounds, program(s) used to solve structures: *SHELXTL* (Sheldrick, 1994); program(s) used to refine structures: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

We thank Dr K. Mackenzie who conceived the research programme, executed preparative and kinetic work, and provided excellent quality crystals. Dr R. Siedlecka is thanked for the preparation of compound (2D). CW thanks the Institut Laue-Langevin for a studentship.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: CF1209). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1998). **C54**, 547–550

Two New Structures of 5-Nitrouracil

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(*Received 17 July 1997; accepted 12 November 1997*)

Abstract

The structure of monoclinic anhydrous 5-nitrouracil, $C_4H_3N_3O_4$, and of the solvate 5-nitrouracil dimethyl sulfoxide, $C_4H_3N_3O_4.C_2H_6OS$, are presented and compared with the previously known structures of the orthorhombic anhydrous form and the monohydrate.

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