C(4)	0.3845 (11)	−0.4477 (5)	0.3198 (2)	0.049 (2)
C(5)	0.3624 (11)	−0.4075 (5)	0.2877 (2)	0.042 (2)
C(6)	0.4886 (13)	−0.4332 (5)	0.2651 (2)	0.052 (2)
C(7)	0.4894 (11)	−0.3975 (4)	0.2322 (1)	0.045 (2)
C(8)	0.3589 (10)	−0.3186 (4)	0.2284 (1)	0.034 (2)
C(9)	0.1621 (11)	−0.3297 (4)	0.2469 (1)	0.038 (2)
C(10)	0.1999 (12)	−0.3445 (5)	0.2827 (2)	0.043 (2)
C(11)	0.0146 (12)	−0.2568 (4)	0.2404 (1)	0.046 (2)
C(12)	−0.0209 (11)	−0.2404 (4)	0.2053 (1)	0.038 (2)
C(13)	0.1772 (11)	−0.2259 (5)	0.1879 (1)	0.039 (2)
C(14)	0.3070 (12)	−0.3056 (5)	0.1936 (2)	0.040 (2)
C(15)	0.4760 (11)	−0.2967 (5)	0.1696 (2)	0.054 (2)
C(16)	0.3885 (10)	−0.2447 (5)	0.1423 (2)	0.046 (2)
C(17)	0.1738 (11)	−0.2241 (5)	0.1515 (2)	0.041 (2)
C(18)	0.2764 (12)	−0.1434 (4)	0.2002 (1)	0.050 (2)
C(19)	0.2604 (14)	−0.2603 (4)	0.2999 (2)	0.068 (3)
C(20)	0.0190 (12)	−0.2865 (5)	0.1373 (1)	0.052 (2)
C(21)	0.0058 (14)	−0.2854 (5)	0.1018 (2)	0.049 (3)
C(22)	0.1290 (15)	−0.3371 (5)	0.0833 (2)	0.075 (3)
C(23)	0.1136 (19)	−0.3325 (7)	0.0508 (3)	0.102 (5)
C(24)	−0.0263 (21)	−0.2844 (8)	0.0367 (2)	0.107 (5)
C(25)	−0.1460 (16)	−0.2327 (6)	0.0548 (2)	0.089 (4)
C(26)	−0.1316 (14)	−0.2348 (6)	0.0868 (2)	0.070 (3)
O(1)	0.2063 (9)	−0.5250 (3)	0.3601 (1)	0.065 (2)
O(2)	0.1132 (8)	−0.1403 (3)	0.1400 (1)	0.052 (2)
O(1*A*)	0.0839 (10)	0.0427 (4)	0.6150 (1)	0.070 (2)
O(2*A*)	0.3922 (11)	−0.1114 (5)	0.3651 (1)	0.074 (2)
C(1*A*)	0.2314 (14)	0.0653 (4)	0.5311 (1)	0.061 (3)
C(2*A*)	0.2327 (13)	0.0811 (4)	0.5666 (1)	0.064 (3)
C(3*A*)	0.0721 (13)	0.0289 (5)	0.5818 (2)	0.055 (3)
C(4*A*)	0.0999 (14)	−0.0661 (5)	0.5747 (1)	0.058 (3)
C(5*A*)	0.1071 (13)	−0.0796 (5)	0.5396 (2)	0.049 (2)
C(6*A*)	−0.0193 (14)	−0.1350 (5)	0.5258 (2)	0.053 (3)
C(7*A*)	−0.0232 (13)	−0.1572 (5)	0.4913 (1)	0.056 (3)
C(8*A*)	0.1629 (12)	−0.1250 (4)	0.4748 (1)	0.043 (2)
C(9*A*)	0.2150 (12)	−0.0342 (5)	0.4851 (1)	0.042 (2)
C(10*A*)	0.2537 (12)	−0.0284 (5)	0.5207 (1)	0.041 (2)
C(11*A*)	0.3827 (13)	0.0066 (5)	0.4656 (1)	0.061 (3)
C(12*A*)	0.3427 (12)	0.0011 (5)	0.4302 (1)	0.055 (2)
C(13*A*)	0.3035	−0.0916	0.4202	0.043
C(14*A*)	0.1268 (12)	−0.1254 (5)	0.4391 (1)	0.042 (2)
C(15*A*)	0.0680 (12)	−0.2090 (4)	0.4231 (1)	0.052 (2)
C(16*A*)	0.1138 (14)	−0.1942 (4)	0.3881 (2)	0.060 (3)
C(17*A*)	0.2236 (12)	−0.1070 (5)	0.3862 (2)	0.050 (2)
C(18*A*)	0.4952 (13)	−0.1442 (5)	0.4245 (2)	0.076 (3)
C(19*A*)	0.4699 (12)	−0.0601 (5)	0.5296 (2)	0.069 (3)
C(20*A*)	0.0886 (13)	−0.0332 (5)	0.3743 (1)	0.052 (2)
C(21*A*)	0.0122 (14)	−0.0463 (5)	0.3411 (2)	0.047 (2)
C(22*A*)	0.1240 (13)	−0.0221 (5)	0.3155 (2)	0.057 (3)
C(23*A*)	0.0555 (15)	−0.0337 (5)	0.2853 (2)	0.057 (3)
C(24*A*)	−0.1266 (16)	−0.0698 (5)	0.2803 (2)	0.063 (3)
C(25*A*)	−0.2418 (14)	−0.0931 (6)	0.3055 (2)	0.080 (3)
C(26*A*)	−0.1740 (14)	−0.0793 (6)	0.3361 (2)	0.070 (3)

Table 2. *Selected geometric parameters* (Å, °)

C(17)—C(13)	1.553 (9)	C(17*A*)—C(13*A*)	1.564 (7)
C(17)—C(16)	1.524 (9)	C(17*A*)—C(16*A*)	1.553 (10)
C(17)—C(20)	1.547 (10)	C(17*A*)—C(20*A*)	1.552 (10)
C(17)—O(2)	1.458 (8)	C(17*A*)—O(2*A*)	1.445 (9)
C(3)—O(1)	1.456 (8)	C(3*A*)—O(1*A*)	1.435 (9)
C(13)—C(17)—O(2)	110.9 (6)	C(13*A*)—C(17*A*)—O(2*A*)	108.5 (6)
C(16)—C(17)—O(2)	111.5 (6)	C(16*A*)—C(17*A*)—O(2*A*)	111.1 (7)
C(20)—C(17)—O(2)	104.5 (6)	C(20*A*)—C(17*A*)—O(2*A*)	106.6 (6)
C(16)—C(17)—C(20)	113.4 (6)	C(16*A*)—C(17*A*)—C(20*A*)	113.4 (6)
C(2)—C(3)—O(1)	111.2 (7)	C(2*A*)—C(3*A*)—O(1*A*)	107.8 (6)

C(12)—C(13)—C(17)—O(2)	82.1 (7)
C(12*A*)—C(13*A*)—C(17*A*)—O(2*A*)	85.8 (6)
C(18)—C(13)—C(17)—O(2)	−43.8 (7)
C(18*A*)—C(13*A*)—C(17*A*)—O(2*A*)	−38.6 (7)
C(15)—C(16)—C(17)—O(2)	145.4 (6)
C(15*A*)—C(16*A*)—C(17*A*)—O(2*A*)	136.6 (6)
C(15)—C(16)—C(17)—C(20)	−97.0 (7)
C(15*A*)—C(16*A*)—C(17*A*)—C(20*A*)	−103.3 (7)
C(16)—C(17)—C(20)—C(21)	−63.8 (9)
C(16*A*)—C(17*A*)—C(20*A*)—C(21*A*)	−62.5 (9)
O(2)—C(17)—C(20)—C(21)	57.8 (8)
O(2*A*)—C(17*A*)—C(20*A*)—C(21*A*)	60.0 (8)
C(1)—C(2)—C(3)—O(1)	−179.1 (6)
C(1*A*)—C(2*A*)—C(3*A*)—O(1*A*)	177.6 (6)

D	H	*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O(1)	H(O1)	O(2)	1.015	1.818	2.798	161.3
O(2)	H(O2)	O(1*A*)	1.074	1.694	2.753	167.9
O(1*A*)	H(O1*A*)	O(1)	0.847	1.936	2.755	163.8

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71505 (17 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: KA1038]

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3,12-Dinitro-5,10,15,20-tetraphenylporphyrin – an Example of a Twisted Intramolecular Charge-Transfer System

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Abstract

The porphyrin ring in the title compound, 10,19-dinitro-2,7,12,17-tetraphenyl-21,22,23,24-tetraazapentacyclo[16.2.1.$1^{3,6}$.$1^{8,11}$.$1^{13,16}$]tetracosa-1,3,5,7,9,11(23),-

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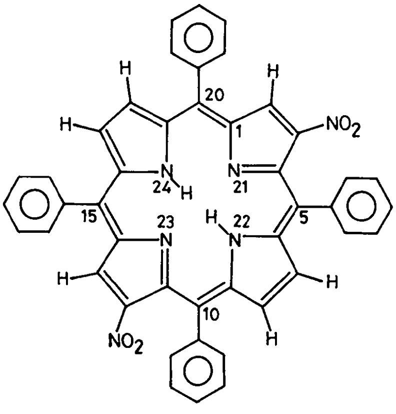
12,14,16,18(21),19-undecaene 0.5-dichloromethane solvate, $C_{44}H_{28}N_6O_4.0.5CH_2Cl_2$, adopts a saddle conformation with neighbouring pyrrole rings tilted with respect to each other. The two nitro groups are situated on alternate pyrrole rings and have their planes angled away from those of the pyrrole rings, thereby indicating that interaction between the porphyrin and nitro groups is slight.

Comment

Nitro porphyrins offer interesting systems for the study of intramolecular charge-transfer states (Gust *et al.*, 1990; Takahashi, Hase, Komura, Imanaga & Ohno, 1992; Rettig, 1986). Structure analysis of the title compound (I) was carried out to determine the orientation of the nitro groups with respect to the porphyrin plane. This structural feature is important to an understanding of the type and magnitude of charge transfer that takes place in the excited state of the system. Moreover, tetraphenyl porphyrins bearing substitutents at the pyrrole C atoms exhibit interesting conformational features (Bhyrappa & Krishnan; 1991; Barkigia *et al.*, 1990; Mandon *et al.*, 1992).



(I)

Details of the synthetic work will be published elsewhere (Dahal & Krishnan, 1993). The structure of (I) is found to be severely nonplanar with an average deviation of 0.36 Å from the mean N_4 plane (the plane passing through the four N atoms of the pyrrole rings). Neighbouring pyrrole rings of the macrocycle are tilted by 26.5 (5), 27.4 (5), 18.4 (4) and 14.8 (4)° with respect to each other, while the opposite pyrroles are tilted by 32.5 (4) and 25.1 (5)° with respect to each other. The displacements of the *meso* C atoms, C5, C10, C15 and C20 from the mean N_4 plane are -0.15 (1), -0.03 (1), -0.02 (1) and 0.21 (1) Å, respectively. These distortions lead to a saddle conformation of the porphyrinoid skeleton similar to those observed for pyrrole-substituted tetraphenyl porphyrins (Bhyrappa, Nethaji & Krishnan, 1993; Mandon *et al.*, 1992). The inner imino H atoms are positioned *trans* to each other on the pyrrole rings not bearing the nitro groups with N—H distances of 1.10 (9) and 0.96 (9) Å (Silvers & Tulinsky, 1967; Chen & Tulinsky, 1971). The phenyl rings adjacent to the nitro groups are rotated by 36.5 (3) and 38.6 (4)° from the mean N_4 plane so as to avoid the steric influence of the nitro groups at positions 3 and 12 of the macrocycle. The other two phenyl rings are rotated by 88.6 (4) and 54.5 (4)° from the mean N_4 plane. The planes of the nitro groups are tilted by 42.2 (6) and 38.0 (9)° with respect to those defined by the pyrrole rings to which they are attached, and deviate by 39.4 (8) and 42.1 (9)° from the mean N_4 plane of the porphyrin. The N atoms of the nitro groups are displaced by 0.27 (1) and 0.38 (1) Å from the plane of the pyrrole rings to which they are attached. The nitro group rotations, coupled with their upward displacements, imply only slight interaction between the porphyrin and nitro groups in the ground state. The compound exhibits a characteristic structureless broad emission and displays a large solvatochromic shift. This suggests a high degree of charge transfer from the porphyrin to the nitro group in the excited state accompanied by the rotation of the nitro group. Efficient charge transfer can occur only when the nitro group is either planar (maximum overlap rule) or perpendicular (minimum overlap rule) to the porphyrin ring. Experimental studies (Dahal & Krishnan, 1993) indicate that the nitro group is more orthogonal in the excited state and the emitting state is a twisted-intramolecular charge-transfer (TICT) state.

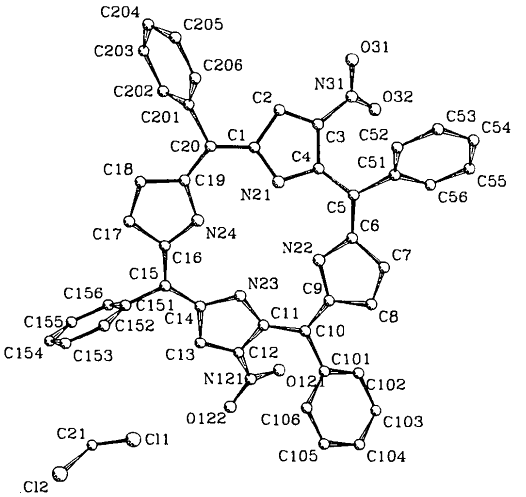


Fig. 1. *PLUTO* (Motherwell & Clegg, 1978) plot of the title porphyrin.

Experimental

Crystal data

$C_{44}H_{28}N_6O_4.0.5CH_2Cl_2$
M_r = 747.25
Triclinic
$P\bar{1}$
a = 12.320 (7) Å
b = 12.524 (7) Å
c = 13.866 (6) Å
α = 75.55 (4)°
β = 69.97 (4)°
γ = 63.86 (3)°
V = 1792 (2) Å^3
Z = 2
D_x = 1.384 Mg m^{-3}

Mo $K\alpha$ radiation
λ = 0.71069 Å
Cell parameters from 25 reflections
θ = 8.26–13.57°
μ = 0.157 mm^{-1}
T = 295 K
Cubic
0.175 × 0.10 × 0.063 mm
Bluish green
Crystal source: slow evaporation from CH_2Cl_2/CH_4O solution

Data collection

Enraf-Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
3699 measured reflections
3344 independent reflections
2109 observed reflections [$F_o > 5.0\sigma(F_o)$]

R_{int} = 0.0241
θ_{max} = 20°
$h = 0 \rightarrow 11$
$k = -12 \rightarrow 12$
$l = -13 \rightarrow 13$
3 standard reflections
frequency: 60 min
intensity variation: <10%

Refinement

Refinement on F
R = 0.075
wR = 0.077
S = 2.7189
2109 reflections
604 parameters
$w = 1/[\sigma^2(F_o) + 0.00001(F_o)^2]$

$(\Delta/\sigma)_{\text{max}}$ = 0.20
$\Delta\rho_{\text{max}}$ = 0.65 e Å^{-3}
$\Delta\rho_{\text{min}}$ = −1.21 e Å^{-3}
Extinction correction: none
Atomic scattering factors from *SHELX*76 (Sheldrick, 1976)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{\text{eq}} = \tfrac{1}{3}\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
C1	0.730 (1)	0.348 (1)	−0.4812 (9)	0.042 (8)
C2	0.836 (1)	0.358 (1)	−0.4692 (9)	0.042 (7)
C3	0.822 (1)	0.339 (1)	−0.3678 (9)	0.039 (7)
C4	0.706 (1)	0.323 (1)	−0.3144 (9)	0.037 (7)
C5	0.647 (1)	0.320 (1)	−0.2072 (9)	0.036 (7)
C6	0.547 (1)	0.286 (1)	−0.1606 (8)	0.040 (7)
C7	0.475 (1)	0.288 (1)	−0.057 (1)	0.049 (8)
C8	0.393 (1)	0.239 (1)	−0.0397 (9)	0.050 (8)
C9	0.409 (1)	0.199 (1)	−0.1345 (9)	0.042 (7)
C10	0.345 (1)	0.142 (1)	−0.1503 (8)	0.035 (7)
C11	0.353 (1)	0.125 (1)	−0.251 (1)	0.033 (6)
C12	0.300 (1)	0.054 (1)	−0.275 (1)	0.038 (7)
C13	0.300 (1)	0.081 (1)	−0.3737 (9)	0.040 (7)
C14	0.361 (1)	0.165 (1)	−0.416 (1)	0.037 (7)
C15	0.382 (1)	0.214 (1)	−0.5184 (9)	0.034 (7)
C16	0.463 (1)	0.273 (1)	−0.5646 (9)	0.035 (7)
C17	0.495 (1)	0.317 (1)	−0.6710 (9)	0.043 (7)
C18	0.586 (1)	0.358 (1)	−0.6900 (8)	0.041 (7)
C19	0.614 (1)	0.342 (1)	−0.5947 (8)	0.036 (7)
C20	0.707 (1)	0.364 (1)	−0.5777 (9)	0.040 (7)
C51	0.692 (1)	0.362 (1)	−0.1421 (8)	0.034 (7)
C52	0.708 (1)	0.467 (1)	−0.1733 (8)	0.042 (7)
C53	0.743 (1)	0.511 (1)	−0.109 (1)	0.047 (8)
C54	0.763 (1)	0.449 (1)	−0.019 (1)	0.049 (8)
C55	0.747 (1)	0.340 (1)	0.0136 (9)	0.047 (8)
C56	0.715 (1)	0.298 (1)	−0.0501 (9)	0.042 (7)
C101	0.258 (1)	0.104 (1)	−0.0592 (9)	0.037 (7)
C102	0.299 (1)	0.032 (1)	0.026 (1)	0.046 (8)
C103	0.216 (1)	−0.005 (1)	0.1127 (9)	0.046 (7)
C104	0.096 (1)	0.027 (1)	0.113 (1)	0.049 (7)
C105	0.055 (1)	0.096 (1)	0.026 (1)	0.051 (8)
C106	0.135 (1)	0.134 (1)	−0.0586 (9)	0.046 (7)
C151	0.316 (1)	0.206 (1)	−0.5848 (9)	0.039 (8)
C152	0.210 (1)	0.292 (1)	−0.6038 (9)	0.044 (7)
C153	0.151 (1)	0.288 (1)	−0.670 (1)	0.051 (8)
C154	0.198 (1)	0.187 (1)	−0.716 (1)	0.063 (9)
C155	0.303 (1)	0.093 (1)	−0.695 (1)	0.079 (10)
C156	0.364 (1)	0.098 (2)	−0.630 (1)	0.079 (10)
C201	0.790 (1)	0.405 (1)	−0.6718 (9)	0.041 (8)
C202	0.864 (1)	0.336 (1)	−0.751 (1)	0.043 (7)
C203	0.940 (1)	0.377 (1)	−0.837 (1)	0.054 (8)
C204	0.945 (1)	0.483 (2)	−0.846 (1)	0.066 (10)
C205	0.872 (2)	0.556 (1)	−0.766 (1)	0.064 (9)
C206	0.793 (1)	0.518 (1)	−0.680 (1)	0.053 (8)
N21	0.6524 (9)	0.3269 (8)	−0.3876 (8)	0.043 (6)
N22	0.5014 (8)	0.2320 (8)	−0.2060 (7)	0.035 (5)
N23	0.3948 (8)	0.1868 (8)	−0.3392 (7)	0.034 (5)
N24	0.5338 (9)	0.2953 (8)	−0.5203 (7)	0.038 (5)
N31	0.924 (1)	0.319 (1)	−0.3254 (9)	0.055 (8)
N121	0.277 (1)	−0.049 (1)	−0.2122 (9)	0.055 (7)
O31	0.986 (1)	0.379 (1)	−0.3665 (8)	0.086 (8)
O32	0.9482 (8)	0.2348 (9)	−0.2575 (8)	0.072 (6)
O121	0.343 (1)	−0.1116 (8)	−0.1535 (7)	0.066 (6)
O122	0.198 (1)	−0.0747 (8)	−0.2254 (7)	0.075 (7)
Cl1	0.0305 (8)	0.0059 (7)	−0.4115 (6)	0.182 (3)
Cl2	−0.115 (2)	0.051 (1)	0.463 (1)	0.219 (6)
C1*S*	0.0	0.0	1/2	0.271 (8)

Table 2. *Selected geometric parameters* (Å, °)

C1—C2	1.44 (1)	C9—C8	1.44 (2)
C1—C20	1.41 (2)	C8—C7	1.32 (2)
C1—N21	1.36 (1)	C7—C6	1.41 (2)
C2—C3	1.33 (2)	C6—C5	1.38 (2)
C3—N31	1.46 (2)	C5—C4	1.41 (2)
C3—C4	1.44 (2)	C5—C51	1.49 (2)
C4—N21	1.37 (2)	C51—C52	1.36 (2)
C12—N121	1.44 (2)	C51—C56	1.38 (2)
N31—O31	1.22 (2)	C52—C53	1.41 (2)
N31—O32	1.22 (1)	C53—C54	1.35 (2)
N121—O121	1.23 (2)	C54—C55	1.40 (2)
N121—O122	1.23 (2)	C55—C56	1.37 (2)
N24—C19	1.38 (2)	C101—C102	1.39 (2)
N24—C16	1.37 (2)	C101—C106	1.39 (2)
N22—C9	1.37 (2)	C102—C103	1.42 (2)
N22—C6	1.40 (2)	C103—C104	1.35 (2)
N23—C14	1.39 (2)	C104—C105	1.40 (2)
N23—C11	1.35 (1)	C105—C106	1.38 (2)
C20—C19	1.39 (2)	C201—C202	1.37 (2)
C20—C201	1.49 (2)	C201—C206	1.41 (2)
C19—C18	1.42 (2)	C202—C203	1.39 (3)
C18—C17	1.36 (2)	C203—C204	1.33 (3)
C17—C16	1.42 (2)	C204—C205	1.40 (2)
C16—C15	1.39 (2)	C205—C206	1.38 (2)
C15—C14	1.38 (2)	C156—C155	1.38 (3)
C15—C151	1.47 (2)	C156—C151	1.43 (2)
C14—C13	1.45 (2)	C155—C154	1.37 (2)
C13—C12	1.33 (2)	C154—C153	1.36 (2)
C12—C11	1.45 (2)	C153—C152	1.37 (2)
C11—C10	1.43 (2)	C152—C151	1.35 (2)
C10—C9	1.38 (2)	Cl2—C1S	1.49 (2)
C10—C101	1.48 (2)		
C1—N21—C4	107 (1)	C9—C8—C7	109 (1)
C19—N24—C16	110 (1)	C8—C7—C6	111 (1)
C9—N22—C6	111 (1)	N22—C6—C7	105 (1)
C14—N23—C11	107 (1)	C7—C6—C5	129 (1)
O32—N31—C3	118 (1)	N22—C6—C5	126 (1)
O31—N31—C3	118 (1)	C6—C5—C5	118 (1)
O122—N121—C12	118 (1)	C6—C5—C4	124 (1)
O121—N121—C12	119 (1)	C4—C5—C5	118 (1)
O121—N121—O122	123 (1)	C3—C4—C5	127 (1)

C2—C3—C4	110 (1)	N21—C4—C5	125 (1)
C3—C2—C1	105 (1)	N21—C4—C3	108 (1)
N21—C1—C2	111 (1)	C5—C51—C56	122 (1)
C2—C1—C20	123 (1)	C5—C51—C52	119 (1)
N21—C1—C20	125 (1)	C52—C51—C56	119 (1)
C1—C20—C201	119 (1)	C51—C52—C53	120 (1)
C1—C20—C19	126 (1)	C52—C53—C54	121 (1)
C19—C20—C201	116 (1)	C53—C54—C55	120 (1)
N24—C19—C20	125 (1)	C54—C55—C56	119 (1)
C20—C19—C18	128 (1)	C51—C56—C55	122 (1)
N24—C19—C18	107 (1)	C10—C101—C10	121 (1)
C19—C18—C17	107 (1)	C102—C101—C10	118 (1)
C18—C17—C16	109 (1)	C101—C102—C10	121 (1)
N24—C16—C17	106 (1)	C102—C103—C104	120 (1)
C17—C16—C15	126 (1)	C103—C104—C105	120 (1)
N24—C16—C15	128 (1)	C104—C105—C106	121 (1)
C16—C15—C151	116 (1)	C101—C106—C105	121 (1)
C16—C15—C14	124 (1)	C20—C201—C206	119 (1)
C14—C15—C151	120 (1)	C20—C201—C202	122 (1)
N23—C14—C15	126 (1)	C202—C201—C206	119 (1)
C15—C14—C13	124 (1)	C201—C202—C203	120 (1)
N23—C14—C13	110 (1)	C202—C203—C204	122 (1)
C14—C13—C12	105 (1)	C203—C204—C205	119 (1)
C13—C12—C11	109 (1)	C204—C205—C206	120 (1)
N23—C11—C12	109 (3)	C201—C206—C205	120 (1)
C12—C11—C10	126 (1)	C155—C156—C151	118 (1)
N23—C11—C10	124 (1)	C156—C155—C154	122 (2)
C11—C10—C101	119 (1)	C155—C154—C153	119 (2)
C11—C10—C9	123 (1)	C154—C153—C152	120 (1)
C9—C10—C101	118 (1)	C153—C152—C151	122 (1)
N22—C9—C10	127 (1)	C156—C151—C152	118 (1)
C10—C9—C8	128 (1)	C15—C151—C152	123 (1)
N22—C9—C8	105 (1)	C15—C151—C156	118 (1)

N21—C1—C20—C201	170 (1)	O31—N31—C3—C2	40 (2)
N22—C6—C5—C51	−172 (1)	O32—N31—C3—C4	36 (2)
N23—C11—C10—C101	158 (1)	O121—N121—C12—C11	−28 (2)
N24—C16—C15—C151	178 (1)	O122—N121—C12—C13	−38 (2)
N31—C3—C4—N21	−167 (1)	C51—C5—C4—N21	−157 (1)
N31—C3—C2—C1	168 (1)	C101—C10—C9—N22	174 (1)
N121—C12—C13—C14	−164 (1)	C151—C15—C14—N23	−165 (1)
N121—C12—C11—N23	161 (1)	C201—C20—C19—N24	175 (1)

The data were collected with a scan width of $(0.90 + 2.70\tan\theta)^\circ$ in ω, a scan rate of 5.5° min^{-1} and a background count for one quarter of the total time spent on each count. The structure was solved using *SHELXS*86 (Sheldrick, 1985) and refined by full-matrix least squares with *SHELX*76 (Sheldrick, 1976). All H atoms apart from H202 and the solvent H atoms were located in the difference map and refined. The high final R is attributed to the small size and poor quality of the crystal specimen.

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Lists of structure factors, anisotropic displacement parameters, least-squares-planes data, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71522 (30 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: MU1041]

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The Structures of *endo*-13-*syn*-Methyltricyclo[8.2.1.0^{2,9}]trideca-5,11-dien-13-*anti*-ol, *endo*-13-*syn*-Methyltricyclo[8.2.1.0^{2,9}]trideca-5,11-dien-13-*anti*-yl Acetate and its Corresponding *endo-endo-anti* Diels–Alder Adducts with 1,2,3,4-Tetrachloro-5,5-dimethoxy-1,3-cyclopentadiene and Hexachlorocyclopentadiene

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Abstract

endo-13-*syn*-Methyltricyclo[8.2.1.0^{2,9}]trideca-5,11-dien-13-*anti*-ol, (1): there are four independent molecules in the asymmetric unit. In two the cyclooctene ring adopts the twist-boat conformation and in the other two, the chair conformation. There are near-

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