

Five 8,11-Substituted Pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecanes

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Abstract. (1) 11-Bromo-11-nitropentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane-8-one, $C_{11}H_{10}BrNO_3$, $M_r = 284.11$, monoclinic, $P2_1/n$, $a = 11.155$ (3), $b = 8.180$ (2), $c = 12.387$ (3) Å, $\beta = 113.54$ (2)°, $V = 1036.2$ (5) Å³, $Z = 4$, $D_x = 1.82$ Mg m⁻³, $\lambda(Cu K\alpha) = 1.54184$ Å, $\mu = 5.39$ mm⁻¹, $F(000) = 568$, $T = 295$ K, $R = 0.038$ for 1384 unique observed reflections. (2) 8,11-Dibromo-8,11-dinitropentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane, $C_{11}H_{10}Br_2N_2O_4$, $M_r = 394.03$, monoclinic, $P2_1$, $a = 6.788$ (2), $b = 13.696$ (4), $c = 6.931$ (2) Å, $\beta = 107.19$ (2)°, $V = 615.5$ (3) Å³, $Z = 2$, $D_x = 2.13$ Mg m⁻³, $\lambda(Cu K\alpha) = 1.54184$ Å, $\mu = 8.58$ mm⁻¹, $F(000) = 384$, $T = 295$ K, $R = 0.041$ for 1003 unique observed reflections. (3) 8,11-Dichloro-8,11-dinitropentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane, $C_{11}H_{10}Cl_2N_2O_4$, $M_r = 305.11$, monoclinic, $P2_1$, $a = 6.773$ (3), $b = 13.579$ (7), $c = 6.834$ (4) Å, $\beta = 107.24$ (4)°, $V = 600.3$ (6) Å³, $Z = 2$, $D_x = 1.69$ Mg m⁻³, $\lambda(Mo K\alpha) = 0.71073$ Å, $\mu = 0.55$ mm⁻¹, $F(000) = 312$, $T = 295$ K, $R = 0.039$ for 969 unique observed reflections. (4) 8,11-Dinitropentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane, $C_{11}H_{12}N_2O_4$, $M_r = 236.22$, monoclinic, $P2_1/c$, $a = 8.530$ (1), $b = 9.909$ (1), $c = 12.277$ (1) Å, $\beta = 96.52$ (2)°, $V = 1031.0$ (2) Å³, $Z = 4$, $D_x = 1.52$ Mg m⁻³, $\lambda(Cu K\alpha) = 1.54184$ Å, $\mu = 0.95$ mm⁻¹, $F(000) = 496$, $T = 295$ K, $R = 0.048$ for 1363 unique observed reflections. (5) 8,8,11,11-Tetranitropentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane, $C_{11}H_{10}N_4O_8$, $M_r = 326.18$, monoclinic, $P2_1/n$, $a = 8.602$ (2), $b = 13.773$ (3), $c = 10.734$ (2) Å, $\beta = 99.73$ (1)°, $V = 1253.5$ (5) Å³, $Z = 4$, $D_x = 1.73$ Mg m⁻³, $\lambda(Mo K\alpha) = 0.71073$ Å, $\mu = 0.14$ mm⁻¹, $F(000) = 672$, $T = 223$ K, $R = 0.046$ for 1361 unique observed reflections. The cage moieties in all five structures are quite similar in that the C—C bonds linking the substituted carbons C(8) and C(11) to the cyclobutane ring are abnormally short [av. 1.516 (7) Å] as are the bonds involving the

bridgehead atom C(4) [av. 1.515 (7) Å], while the C—C cage bond across from the cyclobutane ring [C(9)—C(10)], on the other hand, is longer than normal [av. 1.584 (6) Å].

Introduction. There is considerable current interest in the synthesis and chemistry of new energetic polycyclic 'cage' compounds (*e.g.* Sollott & Gilbert, 1980; Eaton, Ravi Shankar, Price, Pluth, Gilbert, Alster & Sandus, 1984; Marchand & Suri, 1984; Marchand & Reddy, 1984; Paquette, Fisher & Engel, 1985; Paquette, Nakamura & Engel, 1986; Marchand, Sharma, Annapurna & Pednekar, 1987; Marchand, Arney & Dave, 1988; Marchand, 1988; Marchand, Dave, Rajapaksa, Arney, Flippen-Anderson, Gilardi & George, 1989; Marchand, 1989; Zajac, Walters & Woods, 1989). In this connection we have recently synthesized several new substituted pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecanes, (1)–(5). Three of these compounds, (2), (3) and (5), are particularly highly congested in the region between the 8- and 11-positions in the pentacycloundecyl cage system. The structures of these compounds were studied as part of a continuing investigation of the structural parameters of energetic substituents in polynitropolycyclic cage molecules. The structural parameters thereby obtained provide a basis for computational modeling of other molecules in this series that have not yet been synthesized.

Experimental. Table 1 lists the experimental data collection parameters. All data sets were corrected for Lorentz and polarization effects after collection on a Nicolet R3v diffractometer. Compounds (1)–(4) were synthesized at Villanova by Zajac and Walters and compound (5) was synthesized at the University of North Texas by Marchand *et al.* Empirical absorption corrections were applied to data sets (1) and (2) (transmission factors are given in Table 1).

Table 1. *Experimental parameters for molecules (1)–(5)*

	(1)	(2)	(3)	(4)	(5)
Crystal size (mm)	0.07 × 0.30 × 0.35	0.10 × 0.12 × 0.25	0.10 × 0.12 × 0.15	0.05 × 0.40 × 0.50	0.15 × 0.25 × 0.40
Number of reflections used to determine cell parameters and 2θ range(°)	25	25	24	25	23
2θ max (°)	34 < 2θ < 60	33 < 2θ < 78	28 < 2θ < 32	38 < 2θ < 78	26 < 2θ < 34
Data range					
<i>h</i>	0 to 12	−7 to 0	0 to 8	−9 to 9	0 to 9
<i>k</i>	0 to 8	0 to 15	0 to 16	0 to 11	0 to 14
<i>l</i>	−13 to 12	−7 to 7	−8 to 7	−13 to 0	−11 to 11
Standard reflections	400	200	200	400	600
	040	060	060	150	040
	006	003	003	004	004
Variation on standard reflections %	2.7	2.5	2.0	4.0	2.8
2θ scan speed (variable) min./max. (° min ^{−1})	5/30	10/30	8/30	6/30	8/30
Unique reflections	1384, <i>I</i> > σ(<i>I</i>)	1003, <i>I</i> > σ(<i>I</i>)	969, <i>I</i> > σ(<i>I</i>)	1363, <i>I</i> > σ(<i>I</i>)	1361, <i>I</i> > σ(<i>I</i>)
<i>R</i> _{int}	0.01	0.03	0.01	0.01	0.01
<i>g</i> (weight)	0.00023	0.00023	0.00023	0.00025	0.000225
<i>p</i> (secondary extinction)		0.003 (2)	0.032 (4)	0.0010 (2)	
Absorption correction (max./min. transmission)	0.811/0.456	0.86/0.46			
Parameters refined	145	171	212	203	236
Non-hydrogen atoms	Anisotropic	Anisotropic	Anisotropic	Anisotropic	Anisotropic
Hydrogen atoms	Riding	Riding	Isotropic	Isotropic	Coordinates only, <i>B</i> 's fixed
(Δ/σ _{max})	0.001	0.001	0.03	0.002	0.005
<i>R</i>	0.038	0.041	0.039	0.048	0.046
<i>wR</i>	0.050	0.051	0.041	0.052	0.044
<i>S</i>	2.29	2.23	1.67	2.5	1.82
Final difference map excursion (e Å ^{−3})	0.30/−0.38	0.85/−0.45	0.19/−0.23	0.20/−0.21	0.38/−0.37

Since the structure-factor calculations include anomalous dispersion it was possible to use the Rogers η parameter (Rogers, 1981) to give an indication of the absolute configuration for (2) and (3) [$\eta = 0.97$ (14) for (2) and 0.61 (55) for (3)]. All structures were solved by direct methods and refined by full-matrix least-squares on F_o . $\sum w(|F_o| - |F_c|)^2$ minimized where $w = 1/\sigma^2[|F_o| + g(F_o)^2]$, secondary isotropic extinction (when applied) from $F_o^* = F_o/[1.0 + 0.002(p)F_o^2/\sin 2\theta]^{0.25}$. Values used for g and p are given in Table 1. All calculations were performed using the *SHELXTL* system (Sheldrick, 1980).†

Final atomic coordinates and equivalent isotropic displacement parameters are given in Table 2 for molecules (1)–(5), bond lengths and angles are listed in Table 3. Fig. 1 shows the atom numbering used for the cage system and Fig. 2 illustrates the results of the X-ray studies on the five molecules.

Discussion. The cage moieties in all five molecules are structurally very similar. The C—C bonds linking the substituted carbons C(8) and C(11) to the cyclobutane ring are abnormally short [av. 1.516 (7) Å] as are the bonds involving the bridgehead atom C(4) [av. 1.515 (7) Å]. On the other hand, the C—C cage bond across from the cyclobutane ring [C(9)—C(10)] is longer than normal [av. 1.584 (6) Å] while all the

other C—C cage bonds fall into normal ranges [av. 1.551 (7) Å]. The C—C—C angle at C(4) is also significantly smaller than normal [av. 95.2 (4)°]. Similar anomalies have been noted in other structures involving the same pentacyclo ring system (Flippen-Anderson, Gilardi, George, Marchand & Reddy, 1989, and references therein). The major differences between the structures lie in the C(8)⋯C(11) non-bonded intramolecular distances which range from 2.611 in (4) to 2.857 Å in (2). The differences are related to the substitution at these atoms with the separation between the two atoms correlating well with the differences in the crystal volume (Immirzi & Perini, 1977) of the substituent moieties. In (4), which has the smallest C(8)⋯C(11) separation there is only a single NO₂ group on each C atom and they are both equatorial to the ring system. In (1), C(8) is doubly substituted with a Br (equatorial) and an NO₂ group (axial) to the ring system but there is only a carbonyl oxygen on C(11) and the C(8)⋯C(11) approach increases to 2.659 Å. In (2), (3) and (5) both of these atoms are doubly substituted with all three molecules having two NO₂ groups axial to the ring system and approximately parallel to one another. For (5), with two additional equatorial NO₂ groups, the C(8)⋯C(11) distance increases to 2.828 Å; in (3), with Cl atoms equatorial to the cage, the distance is 2.846 Å and the largest separation (2.857 Å) is found in (2) where the other two equatorial substituents are Br atoms. Another unusual, yet consistent, departure from 'normal geometry' is noted in (5) which has two geminal dinitro groups. The C—N distances for the axial nitro groups aver-

† Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53412 (35 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($\text{\AA}^2 \times 10^3$)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

(1)	x	y	z	U_{eq}
C(11)	667 (3)	5369 (4)	3016 (3)	37 (1)
C(1)	1194 (3)	4172 (4)	2385 (3)	37 (1)
C(7)	88 (4)	3447 (4)	1259 (3)	42 (1)
C(8)	-1215 (4)	4128 (4)	1105 (3)	41 (1)
C(9)	-1387 (3)	3609 (4)	2210 (3)	40 (1)
C(10)	-264 (3)	4325 (4)	3346 (3)	37 (1)
C(3)	569 (3)	2801 (4)	3895 (3)	44 (1)
C(2)	1267 (3)	2550 (4)	3057 (3)	44 (1)
C(6)	164 (4)	1824 (4)	1937 (3)	45 (1)
C(5)	-1020 (4)	1774 (4)	2285 (3)	46 (1)
C(4)	-412 (5)	1406 (4)	3591 (4)	54 (2)
Br(11)	2072 (1)	6269 (1)	4401 (1)	66 (1)
N(11)	32 (3)	6885 (3)	2296 (3)	45 (1)
O(11a)	500 (3)	7429 (3)	1641 (3)	63 (1)
O(11b)	-902 (3)	7457 (3)	2434 (3)	73 (2)
O(8)	-1983 (3)	4858 (3)	275 (2)	59 (1)
(2)				
C(11)	2098 (14)	10627 (7)	-952 (13)	41 (3)
C(1)	684 (13)	10389 (7)	335 (14)	44 (3)
C(7)	1592 (14)	9667 (7)	2101 (15)	45 (3)
C(8)	3761 (13)	9308 (7)	2318 (13)	42 (3)
C(9)	3528 (14)	8883 (7)	227 (13)	41 (3)
C(10)	2618 (14)	9614 (6)	-1579 (13)	39 (3)
C(3)	387 (14)	9211 (7)	-2534 (14)	45 (3)
C(2)	-641 (14)	9542 (8)	-924 (14)	44 (3)
C(6)	241 (13)	8826 (7)	801 (13)	43 (3)
C(5)	1689 (14)	8174 (8)	30 (14)	47 (3)
C(4)	613 (17)	8108 (7)	-2193 (16)	55 (4)
Br(11)	555 (2)	11370	-3328 (2)	66 (1)
N(11)	3879 (13)	11308 (8)	-95 (13)	52 (3)
O(11a)	3641 (14)	11937 (7)	1033 (16)	81 (4)
O(11b)	5411 (13)	11189 (6)	-574 (14)	71 (4)
Br(8)	4535 (2)	8246 (1)	4376 (2)	67 (1)
N(8)	5487 (13)	10024 (7)	3137 (11)	51 (3)
O(8a)	5247 (14)	10619 (8)	4336 (15)	90 (4)
O(8b)	7033 (11)	9943 (8)	2619 (12)	75 (3)
(3)				
C(1)	4385 (7)	6944 (4)	4738 (8)	37 (2)
C(2)	5690 (7)	6077 (4)	5980 (8)	41 (2)
C(3)	4689 (8)	5736 (4)	7617 (8)	44 (2)
C(4)	4398 (12)	4645 (5)	7277 (10)	55 (2)
C(5)	3336 (9)	4720 (5)	4998 (8)	47 (2)
C(6)	4786 (8)	5371 (5)	4211 (8)	41 (2)
C(7)	3466 (7)	6229 (4)	2912 (7)	36 (2)
C(8)	1288 (7)	5874 (4)	2727 (7)	40 (2)
Cl(8)	558 (3)	4920 (2)	790 (2)	69 (1)
N(8)	-439 (6)	6607 (5)	1876 (6)	53 (2)
O(8a)	-227 (7)	7201 (5)	646 (8)	92 (2)
O(8b)	-1984 (6)	6518 (5)	2386 (6)	74 (2)
C(9)	1513 (7)	5441 (4)	4813 (7)	38 (2)
C(10)	2475 (7)	6175 (4)	6684 (7)	36 (2)
C(11)	3014 (7)	7190 (4)	6032 (8)	39 (2)
Cl(11)	4458 (3)	7868	8253 (2)	66 (1)
N(11)	1216 (7)	7882 (4)	5173 (7)	51 (2)
O(11a)	-299 (7)	7769 (4)	5713 (8)	77 (2)
O(11b)	1438 (7)	8520 (4)	4006 (9)	84 (2)
(4)				
C(11)	4521 (3)	342 (2)	2310 (2)	53 (1)
N(11)	5487 (2)	701 (2)	1386 (2)	68 (1)
O(11a)	5388 (3)	1838 (2)	1008 (2)	102 (1)
O(11b)	6281 (2)	-186 (3)	1053 (2)	95 (1)
C(1)	3926 (3)	1570 (2)	2861 (2)	61 (1)
C(7)	2971 (3)	1137 (2)	3819 (2)	61 (1)
C(8)	2929 (3)	-392 (2)	3906 (2)	52 (1)
N(8)	2122 (3)	-836 (2)	4875 (2)	65 (1)
O(8a)	2721 (3)	-493 (3)	5774 (2)	105 (1)
O(8b)	918 (3)	-1497 (2)	4741 (2)	98 (1)
C(9)	2023 (3)	-766 (2)	2813 (2)	49 (1)
C(10)	2980 (3)	-333 (2)	1843 (2)	48 (1)
C(3)	1975 (3)	841 (2)	1306 (2)	55 (1)
C(2)	2359 (3)	1960 (2)	2167 (2)	62 (1)
C(6)	1412 (3)	1529 (2)	3115 (2)	63 (1)
C(5)	604 (3)	213 (3)	2680 (2)	58 (1)
C(4)	296 (3)	434 (3)	1453 (2)	64 (1)

Table 2 (cont.)

	x	y	z	U_{eq}
(5)				
C(1)	-981 (4)	3424 (2)	3261 (3)	27 (1)
C(2)	-449 (4)	2455 (2)	2716 (3)	29 (1)
C(3)	-816 (4)	2522 (2)	1256 (3)	26 (1)
C(4)	721 (4)	2264 (2)	832 (3)	34 (1)
C(5)	1696 (4)	2994 (2)	1689 (3)	30 (1)
C(6)	1296 (4)	2787 (2)	3015 (3)	31 (1)
C(7)	774 (4)	3761 (2)	3566 (3)	26 (1)
C(8)	1262 (3)	4481 (2)	2649 (3)	25 (1)
C(9)	821 (3)	3972 (2)	1381 (3)	23 (1)
C(10)	-968 (3)	3644 (2)	1067 (3)	22 (1)
C(11)	-1926 (3)	3886 (2)	2092 (3)	24 (1)
N(11a)	-2443 (3)	4929 (2)	2202 (3)	34 (1)
O(11a)	-2882 (4)	5364 (2)	1210 (3)	71 (1)
O(11b)	-2464 (3)	5248 (2)	3244 (2)	52 (1)
N(11b)	-3563 (3)	3382 (2)	1765 (3)	36 (1)
O(11c)	-4090 (3)	3018 (2)	2624 (2)	59 (1)
O(11d)	-4212 (3)	3396 (2)	675 (3)	69 (1)
N(8a)	761 (3)	5532 (2)	2744 (3)	30 (1)
O(8a)	321 (4)	5969 (2)	1770 (2)	67 (1)
O(8b)	855 (3)	5871 (2)	3788 (2)	50 (1)
N(8b)	3075 (3)	4622 (2)	2923 (3)	36 (1)
O(8c)	3798 (3)	4310 (2)	3910 (3)	56 (1)
O(8d)	3645 (3)	5059 (2)	2122 (3)	61 (1)

Table 3. Bond lengths (\AA) and bond angles ($^\circ$)

	(1)	(2)	(3)	(4)	(5)
C(1)—C(2)	1.551 (5)	1.566 (13)	1.563 (7)	1.550 (3)	1.557 (4)
C(1)—C(11)	1.511 (6)	1.525 (15)	1.498 (8)	1.508 (3)	1.515 (4)
C(1)—C(7)	1.564 (4)	1.552 (13)	1.557 (7)	1.564 (4)	1.560 (4)
C(2)—C(3)	1.540 (6)	1.548 (15)	1.541 (9)	1.540 (3)	1.548 (4)
C(2)—C(6)	1.557 (4)	1.525 (13)	1.522 (7)	1.551 (4)	1.550 (5)
C(3)—C(4)	1.521 (6)	1.531 (14)	1.504 (9)	1.519 (3)	1.512 (5)
C(3)—C(10)	1.541 (5)	1.563 (12)	1.563 (7)	1.547 (3)	1.562 (4)
C(4)—C(5)	1.514 (6)	1.500 (13)	1.513 (8)	1.516 (4)	1.517 (4)
C(5)—C(6)	1.544 (7)	1.536 (15)	1.532 (9)	1.541 (3)	1.546 (5)
C(5)—C(9)	1.549 (5)	1.555 (14)	1.550 (8)	1.545 (3)	1.551 (4)
C(6)—C(7)	1.556 (5)	1.578 (13)	1.573 (7)	1.551 (3)	1.562 (4)
C(7)—C(8)	1.496 (6)	1.517 (13)	1.521 (7)	1.520 (3)	1.506 (4)
C(8)—C(9)	1.516 (6)	1.526 (13)	1.508 (7)	1.517 (3)	1.521 (4)
C(9)—C(10)	1.576 (4)	1.579 (12)	1.600 (7)	1.578 (3)	1.585 (4)
C(10)—C(11)	1.521 (6)	1.526 (13)	1.526 (8)	1.527 (3)	1.519 (4)
C(11)—N(11)	1.526 (4)	1.504 (13)	1.512 (7)	1.517 (3)	1.513 (4)
C(8)—N(8)		1.502 (12)	1.515 (7)	1.506 (3)	1.518 (4)
C(11)—X	1.948 (3) ^a	1.956 (09) ^b	1.797 (5) ^c		1.557 (4) ^d
C(8)—X	1.202 (4) ^a	1.996 (09)	1.812 (6)		1.550 (4)
N—O	1.212 (6)	1.205 (15)	1.203 (7)	1.218 (3)	1.205 (4)
	1.215 (5)	1.209 (14)	1.199 (7)	1.209 (3)	1.208 (4)
		1.193 (14)	1.203 (7)	1.211 (3)	1.205 (4)
		1.211 (12)	1.217 (8)	1.213 (3)	1.218 (4)
					1.224 (4)
					1.203 (4)
					1.211 (4)
					1.213 (4)
C(7)—C(1)—C(2)	90.5 (2)	89.8 (7)	89.7 (4)	89.5 (2)	89.9 (2)
C(2)—C(1)—C(11)	103.3 (3)	100.9 (8)	101.4 (4)	105.2 (2)	101.5 (2)
C(7)—C(1)—C(11)	112.1 (3)	115.2 (8)	116.2 (4)	110.3 (2)	114.4 (3)
C(1)—C(2)—C(3)	108.4 (3)	108.1 (8)	108.7 (4)	107.5 (2)	107.9 (2)
C(1)—C(2)—C(6)	89.7 (6)	90.7 (8)	90.7 (4)	90.5 (2)	90.3 (2)
C(3)—C(2)—C(6)	102.7 (3)	102.8 (8)	103.1 (4)	103.2 (2)	102.6 (3)
C(2)—C(3)—C(10)	100.9 (3)	100.3 (7)	99.5 (4)	110.6 (2)	100.8 (2)
C(4)—C(3)—C(10)	104.5 (3)	104.0 (7)	104.3 (5)	103.6 (2)	104.6 (3)
C(2)—C(3)—C(4)	103.9 (3)	103.0 (9)	104.5 (5)	103.9 (2)	104.5 (2)
C(3)—C(4)—C(5)	94.9 (3)	95.4 (8)	95.5 (5)	95.5 (2)	94.8 (2)
C(4)—C(5)—C(6)	103.6 (3)	103.1 (7)	104.0 (5)	104.0 (2)	104.4 (3)
C(4)—C(5)—C(9)	104.6 (3)	105.2 (8)	104.5 (5)	103.9 (2)	104.4 (2)
C(6)—C(5)—C(9)	101.3 (3)	100.7 (8)	100.7 (5)	100.4 (2)	100.4 (3)
C(2)—C(6)—C(7)	90.5 (3)	90.3 (7)	90.5 (4)	90.0 (2)	90.1 (2)
C(5)—C(6)—C(7)	107.7 (3)	107.4 (7)	108.0 (4)	107.6 (2)	108.3 (2)
C(2)—C(6)—C(5)	102.8 (3)	104.1 (8)	103.5 (5)	102.9 (2)	102.8 (2)
C(1)—C(7)—C(8)	110.6 (3)	115.6 (9)	114.3 (4)	110.2 (2)	115.2 (2)
C(6)—C(7)—C(8)	103.1 (4)	101.7 (8)	100.8 (4)	105.2 (2)	100.9 (3)
C(6)—C(7)—C(1)	89.3 (2)	89.2 (6)	89.1 (3)	90.0 (2)	89.7 (2)
C(7)—C(8)—C(9)	104.4 (3)	101.8 (7)	102.8 (3)	101.3 (2)	103.0 (2)
C(7)—C(8)—X	128.1 (4) ^e	110.5 (7) ^b	109.6 (4) ^c		110.0 (2) ^d
C(7)—C(8)—N(8)		116.8 (8)	116.3 (5)	111.3 (2)	118.1 (3)
C(9)—C(8)—X	127.4 (4) ^e	109.4 (6) ^b	109.9 (4) ^c		108.5 (2) ^d
C(9)—C(8)—N(8)		117.2 (8)	118.0 (5)	113.2 (2)	117.9 (2)
N(8)—C(8)—X		101.2 (5)	100.2 (3) ^f		99.0 (2) ^d
C(5)—(9)—C(10)	102.1 (2)	102.1 (6)	101.7 (4)	102.5 (2)	102.5 (2)
C(5)—C(9)—C(8)	101.5 (3)	100.2 (8)	100.3 (4)	104.7 (2)	99.8 (2)
C(8)—C(9)—C(10)	111.1 (3)	114.6 (8)	114.5 (5)	110.2 (2)	114.1 (3)

Table 3 (cont.)

	(1)	(2)	(3)	(4)	(5)
C(3)—C(10)—C(11)	102.5 (3)	99.5 (7)	100.4 (4)	104.0 (2)	99.6 (2)
C(9)—C(10)—C(11)	110.7 (3)	114.8 (7)	113.9 (4)	109.5 (2)	114.2 (2)
C(9)—C(10)—C(3)	102.6 (3)	102.4 (7)	101.7 (4)	102.5 (2)	101.4 (2)
C(1)—C(11)—C(10)	102.9 (3)	102.2 (8)	102.4 (4)	101.7 (2)	103.1 (2)
C(1)—C(11)—X	111.0 (2) ^a	109.3 (6) ^b	109.6 (3) ^c	117.2 (2) ^d	117.2 (2) ^d
C(10)—C(11)—X	111.8 (2) ^a	110.1 (6) ^b	109.5 (3) ^c	117.9 (3)	117.9 (2) ^d
C(1)—C(11)—N(11)	114.2 (3)	118.2 (8)	118.6 (4)	112.7 (2)	109.7 (2)
C(10)—C(11)—N(11)	114.0 (3)	116.7 (8)	116.1 (4)	109.8 (2)	108.6 (2)
N(11)—C(11)—X	103.3 (2) ^a	100.2 (6) ^b	100.6 (4) ^c	117.0 (2)	100.0 (2) ^d
C(8)—N(8)—O		116.8 (9)	118.0 (5)	117.0 (2)	117.9 (3)
		118.4 (9)	117.5 (5)	120.4 (2)	117.2 (3)
				118.1 (3)	118.1 (3)
				116.1 (2)	116.1 (2)
O—N(8)—O		124.8 (10)	124.3 (5)	122.6 (2)	124.9 (3)
				125.7 (3)	125.7 (3)
C(11)—N(11)—O	117.8 (3)	116.9 (9)	117.8 (5)	118.8 (2)	116.6 (3)
	117.0 (4)	118.1 (9)	117.1 (5)	117.1 (2)	118.0 (3)
				117.6 (3)	117.6 (3)
				117.2 (2)	117.2 (2)
O—N(11)—O	125.1 (3)	125.0 (10)	125.2 (5)	124.1 (3)	125.3 (3)
				125.2 (3)	125.2 (3)

Notes: (a) X = O, (b) X = Br, (c) X = Cl, (d) X = N.

age 1.515 (4) Å while the average value for the corresponding equatorial nitro groups is 1.554 (4) Å. Similar distances were found in the hexanitro analog of (5) (Marchand, Dave, Rajapaksa, Arney, Flippen-

Anderson, Gilardi & George, 1989). It should be noted, however, that in (4), which has only the two equatorial NO₂ groups, the average C—N distance is 1.512 (3) Å while in (1), which has only a single NO₂ group axial to the ring system, the C—N distance is intermediate between the two values at 1.526 (4) Å.

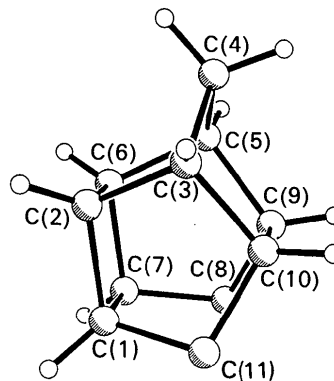


Fig. 1. The numbering scheme used for the cage portion of all five molecules.

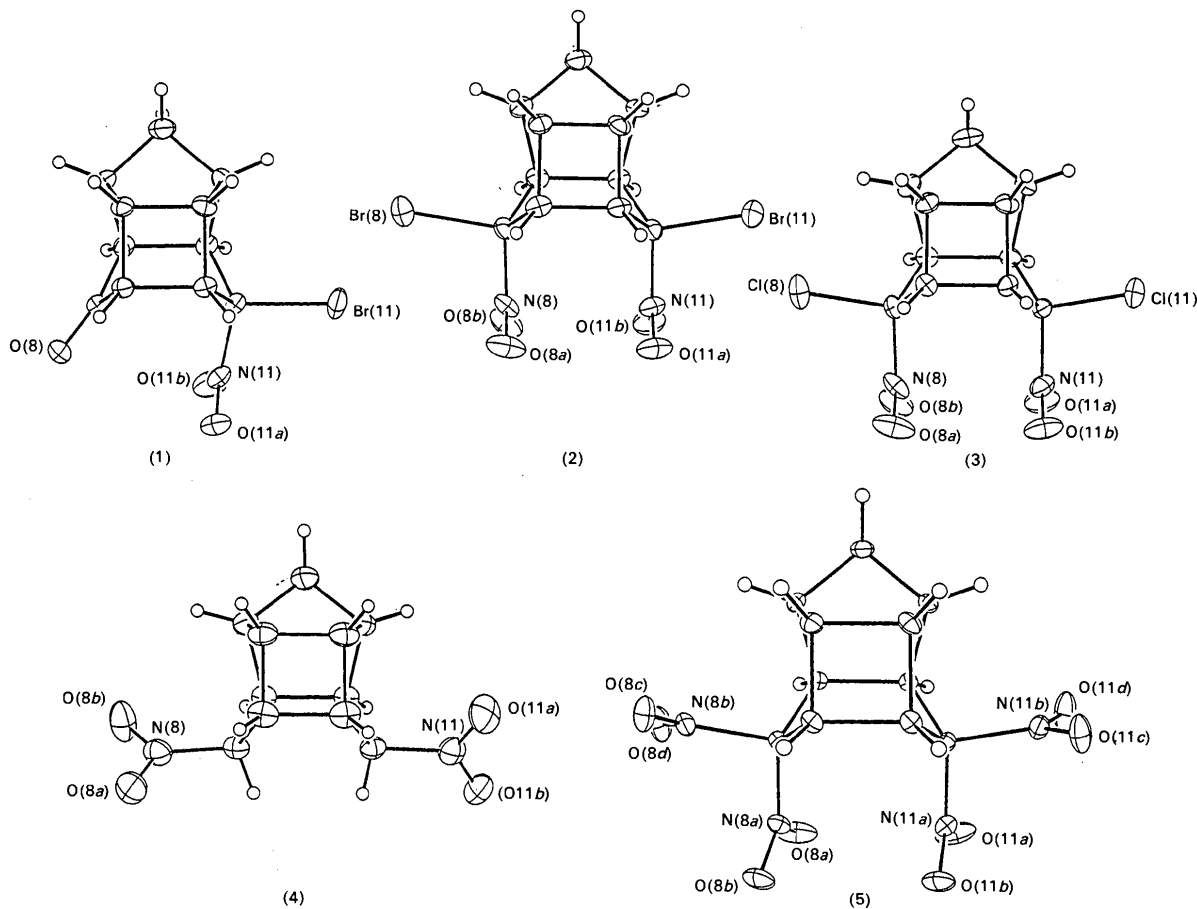


Fig. 2. The results of the X-ray studies on molecules (1)–(5). The thermal ellipsoids are shown at the 20% probability level.

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Structures of Three Photochromic Compounds and Three Non-Photochromic Derivatives; the Effect of Methyl Substituents

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Abstract. (1) 1,3,3-Trimethylspiro{indoline-2,3'-(3'H)-[1,4]oxazino(3'H)-[3,2-f][quindine}, $C_{21}H_{19}N_3O$, $M_r = 329.4$, monoclinic, $P2_1/n$, $a = 10.999$ (1), $b = 14.983$ (1), $c = 21.351$ (2) Å, $\beta = 97.259$ (8)°, $V = 3490.4$ Å³, $Z = 8$, $D_x = 1.253$ g cm⁻³, $\lambda(\text{Cu } K\alpha) = 1.54184$ Å, $\mu = 5.9$ cm⁻¹, $F(000) = 1392$, $T = 295$ K, $R = 0.064$ for 3999 unique observed reflections. (2) 1,2',3,3-Tetramethylspiro{indoline-2,3'(3'H)-[1,4]-oxazino[3,2-f]quindine}, $C_{22}H_{21}N_3O$, $M_r = 343.4$, monoclinic, $P2_1/c$, $a = 7.3093$ (4), $b = 22.3464$ (14), $c = 10.9473$ (8) Å, $\beta = 94.848$ (5)°, $V = 1781.7$ Å³, $Z = 4$, $D_x = 1.280$ g cm⁻³, $\mu(\text{Cu } K\alpha) = 6.0$ cm⁻¹, $F(000) = 728$, $T = 295$ K, $R = 0.043$ for 2574 unique observed reflections. (3) 5-Methoxy-1,3,3-trimethylspiro{indoline-2,3'(3'H)-[1,4]oxazino[3,2-f]-quindine}, $C_{22}H_{21}N_3O_2$, $M_r = 359.4$, monoclinic, $P2_1/n$, $a = 11.5201$ (5), $b = 10.7143$ (5), $c = 16.0914$ (7) Å, $\beta = 108.075$ (4)°, $V = 1888.1$ Å³, $Z = 4$, $D_x = 1.264$ g cm⁻³, $\mu(\text{Cu } K\alpha) = 6.3$ cm⁻¹, $F(000) = 760$, $T = 295$ K, $R = 0.061$ for 2091 unique observed reflections. (4) 5-Methoxy-1,2',3,3-tetramethylspiro{indoline-2,3'(3'H)-[1,4]oxazino[3,2-f]-quindine}, $C_{23}H_{23}N_3O_2$, $M_r = 373.5$, monoclinic, $P2_1/n$, $a = 9.9249$ (5), $b = 16.7437$ (8), $c = 24.0188$ (8) Å, $\beta = 100.299$ (3)°, $V = 3927.1$ Å³, $Z = 8$, $D_x = 1.263$ g cm⁻³, $\mu(\text{Cu } K\alpha) = 6.2$ cm⁻¹, $F(000) = 1584$, $T = 295$ K, $R = 0.062$ for 3246 unique observed reflections. (5) 1',3',3'-Trimethyl-6-nitrospiro[benzopyran-2(2H),2'-indoline], $C_{19}H_{18}N_2O_3$, $M_r = 322.4$, monoclinic, $P2_1/n$, $a = 16.146$ (1), $b = 10.979$ (1), $c = 19.728$ (1) Å, $\beta = 105.826$ (5)°, $V = 3364.6$ Å³, $Z = 8$, $D_x = 1.273$ g cm⁻³, $\mu(\text{Cu } K\alpha) =$