Table 2. *Selected bond distances (Å), bond angles (°), and torsion angles (°)*

E.s.d.'s lie in the ranges 0·002–0·003 Å and 0·1–0·2°.

C(1)–C(7)	1·461		
C(1)–C(2)	1·405	C(7)–C(8)	1·411
C(2)–C(3)	1·386	C(8)–C(9)	1·391
C(3)–C(4)	1·369	C(9)–C(10)	1·369
C(4)–C(5)	1·382	C(10)–C(11)	1·385
C(5)–C(6)	1·385	C(11)–C(12)	1·390
C(6)–C(1)	1·426	C(7)–C(12)	1·415
C(6)–C(100)	1·507	C(12)–C(200)	1·509
C(2)–N(1)	1·422	C(8)–N(2)	1·417
N(1)–O(1)	1·254	N(2)–O(2)	1·265
N(1)–N(2)	1·339		

C(7)–C(1)–C(6)	127·1	C(1)–C(7)–C(12)	126·4
C(1)–C(6)–C(100)	124·0	C(7)–C(12)–C(200)	123·8
C(1)–C(6)–C(5)	118·8	C(7)–C(12)–C(11)	118·8
C(5)–C(6)–C(100)	116·8	C(11)–C(12)–C(200)	116·9
C(6)–C(5)–C(4)	122·5	C(12)–C(11)–C(10)	122·2
C(5)–C(4)–C(3)	119·8	C(11)–C(10)–C(9)	120·1
C(4)–C(3)–C(2)	118·3	C(10)–C(9)–C(8)	118·2
C(3)–C(2)–C(1)	123·6	C(9)–C(8)–C(7)	123·0
C(2)–C(1)–C(6)	115·9	C(8)–C(7)–C(12)	116·5
C(1)–C(2)–N(1)	120·4	C(7)–C(8)–N(2)	120·3
C(2)–N(1)–C(2)	119·3	C(8)–N(2)–N(1)	119·6
N(2)–N(1)–O(1)	118·3	N(1)–N(2)–O(2)	117·6
C(2)–N(1)–O(1)	121·7	C(8)–N(2)–O(2)	121·7
C(2)–C(1)–C(7)	116·9	C(8)–C(7)–C(1)	116·9

C(100)–C(6)–C(1)–C(7)	–13·4	C(1)–C(7)–C(12)–C(200)	–13·7
C(6)–C(1)–C(7)–C(12)	–32·7		
C(2)–C(1)–C(7)–C(8)	–23·3		
C(2)–N(1)–N(2)–C(8)	–23·9		
O(1)–N(1)–N(2)–O(2)	–2·7		
C(7)–C(1)–C(2)–N(1)	11·5	C(1)–C(7)–C(8)–N(2)	12·6
C(1)–C(2)–N(1)–N(2)	12·3	C(7)–C(8)–N(2)–N(1)	11·2

Discussion. The molecule has an approximate, non-crystallographic twofold rotation axis. It is distorted from planarity to relieve the steric repulsion between the methyl groups [C(100)···C(200), 3·03 Å]. The major distortions are in the torsion angles involving C–CH$_3$ bonds and in those involving the C atoms of the diazine ring, the atoms C(100)–C(6)–C(1)–C(7)–C(12)–C(200) forming a pronounced spiral. The diazine ring has a nearly perfect twist conformation. In spite of these distortions, the bond lengths and angles in the dinitroso moiety do not differ much from those observed in unstrained dinitroso groupings (Prout, Stothard & Watkin, 1978). The N–N bond distance of 1·339 (2) Å is slightly longer than usual (1·29–1·32 Å). There are no unusually short intermolecular contacts.

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4,5-Dichloro-9,10-diazaphenanthrene N,N'-Dioxide

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Abstract. C$_{12}$H$_6$Cl$_2$N$_2$O$_2$, M_r = 281·10, triclinic, $P\bar{1}$, a = 7·419 (2), b = 9·652 (2), c = 16·662 (4) Å, α = 90·34 (2), β = 96·50 (2), γ = 106·04 (2)°, Z = 4, D_m = 1·62, D_x = 1·64 Mg m^{-3}. R = 0·032 for 3123 observed reflexions. The molecule exists as 4,5-dichloro-9,10-diazaphenanthrene N,N'-dioxide (not as 2,2'-dichloro-6,6'-dinitrosobiphenyl). The two independent molecules in the asymmetric unit have nearly identical structural parameters, which are similar to those of 4,5-dimethyl-9,10-diazaphenanthrene N,N'-dioxide [Whittleton & Dunitz (1982). *Acta Cryst.* B38, 2054–2055].

Introduction. This work forms part of a projected study of the nitroso dimerization pathway. The title compound (Fig. 1) was prepared by the method described in Whittleton & Dunitz (1982) (WD). Intensity collection [4009 reflexions, 3123 with $I > 3\sigma(I)$],

Table 1. *Final atomic parameters* ($\times 10^4$) *with e.s.d.'s in parentheses*

For the heavy atoms U is $\frac{1}{3}$TrU after transformation of U_{ij} components to Cartesian axes.

	x	y	z	U (Å²)
C(1)	2316 (3)	2608 (3)	3324 (2)	386 (7)
C(2)	2490 (4)	2344 (3)	2505 (2)	494 (8)
C(3)	2575 (4)	3384 (5)	1923 (2)	630 (10)
C(4)	2416 (5)	4693 (4)	2132 (2)	667 (12)
C(5)	2039 (4)	4967 (3)	2905 (2)	583 (11)
C(6)	1941 (4)	3929 (3)	3479 (2)	438 (8)
C(7)	2422 (3)	1468 (3)	3879 (2)	399 (7)
C(8)	1986 (4)	57 (3)	3546 (2)	515 (9)
C(9)	1730 (5)	−1147 (3)	4011 (3)	683 (11)
C(10)	2024 (5)	−965 (4)	4824 (3)	732 (12)
C(11)	2752 (5)	406 (4)	5187 (2)	600 (11)
C(12)	2992 (4)	1593 (3)	4716 (2)	448 (8)
Cl(1)	1064 (1)	4260 (1)	4361 (1)	557 (2)
Cl(2)	4369 (1)	3226 (1)	5165 (1)	569 (2)
N(1)	2544 (4)	976 (3)	2246 (2)	619 (9)
N(2)	1977 (4)	−153 (3)	2699 (2)	629 (9)
O(1)	2934 (5)	761 (4)	1556 (2)	1057 (13)
O(2)	1733 (4)	−1398 (3)	2391 (2)	963 (12)
H(3)	2798 (46)	3149 (35)	1454 (19)	626 (92)
H(4)	2373 (56)	5469 (43)	1734 (24)	889 (124)
H(5)	1730 (52)	5817 (40)	3014 (22)	798 (113)
H(9)	1352 (58)	−2084 (44)	3782 (25)	1034 (130)
H(10)	1794 (53)	−1719 (40)	5107 (23)	823 (114)
H(11)	3109 (46)	512 (35)	5736 (20)	655 (95)
C(1')	2604 (3)	6258 (3)	8311 (2)	382 (7)
C(2')	2895 (4)	6579 (3)	7505 (2)	457 (8)
C(3')	3056 (4)	5573 (4)	6935 (2)	566 (10)
C(4')	2820 (5)	4182 (4)	7152 (2)	616 (11)
C(5')	2302 (4)	3769 (3)	7905 (2)	564 (10)
C(6')	2139 (4)	4774 (3)	8466 (2)	442 (8)
C(7')	2632 (3)	7447 (3)	8857 (2)	401 (8)
C(8')	2260 (4)	8675 (3)	8505 (2)	467 (8)
C(9')	1956 (5)	9791 (3)	8957 (2)	596 (11)
C(10')	2153 (5)	9742 (3)	9774 (2)	618 (11)
C(11')	2794 (4)	8665 (3)	10157 (2)	538 (10)
C(12')	3081 (4)	7569 (3)	9703 (2)	436 (8)
N(1')	2973 (4)	7969 (3)	7233 (2)	549 (9)
N(2')	2321 (3)	8858 (3)	7662 (2)	542 (8)
O(1')	3428 (4)	8336 (3)	6551 (2)	876 (11)
O(2')	2052 (4)	9971 (3)	7334 (2)	799 (10)
Cl(1')	1041 (1)	4097 (1)	9300 (1)	567 (2)
Cl(2')	4327 (1)	6484 (1)	10197 (1)	582 (2)
H(3')	1896 (50)	2834 (38)	8014 (22)	770 (106)
H(4')	2933 (57)	3471 (44)	6756 (25)	960 (130)
H(5')	3350 (46)	5907 (35)	6443 (20)	596 (92)
H(9')	1669 (51)	10533 (39)	8673 (22)	784 (110)
H(10')	1946 (46)	10436 (35)	10042 (20)	655 (93)
H(11')	1669 (51)	10533 (39)	8673 (22)	784 (110)

structure analysis, and refinement were as described in WD; final $R = 0.032$, $R_w = 0.038$. Positional and equivalent isotropic vibrational parameters ($\frac{1}{3}$TrU) are given in Table 1, selected bond lengths, bond angles, and torsion angles in Table 2;* C—H distances lie in the range 0.86–1.00 Å.

Table 2. *Selected bond distances* (Å), *bond angles* (°) *and torsion angles* (°)

For each molecular parameter, the first number refers to the unprimed atoms in Table 1, the second to the primed atoms. Since the unprimed and primed molecules have opposite sense of chirality, the signs of the torsion angles of the primed molecule have been reversed for consistency. E.s.d.'s are 0.003–0.005 Å for lengths and 0.2–0.3° for angles.

C(1)–C(2)	1.413, 1.408		C(7)–C(8)	1.405, 1.406	
C(2)–C(3)	1.394, 1.392		C(8)–C(9)	1.383, 1.392	
C(3)–C(4)	1.349, 1.362		C(9)–C(10)	1.350, 1.355	
C(4)–C(5)	1.387, 1.382		C(10)–C(11)	1.391, 1.388	
C(5)–C(6)	1.383, 1.382		C(11)–C(12)	1.374, 1.374	
C(6)–C(1)	1.407, 1.411		C(12)–C(7)	1.406, 1.408	
C(2)–N(1)	1.399, 1.407		C(8)–N(2)	1.423, 1.421	
N(1)–O(1)	1.247, 1.247		N(2)–O(2)	1.262, 1.263	
C(6)–Cl(1)	1.736, 1.731		C(12)–Cl(2)	1.735, 1.733	
C(1)–C(7)	1.455, 1.453				
N(1)–N(2)	1.329, 1.336				

C(7)–C(1)–C(6)	128.6, 127.9		C(1)–C(7)–C(12)	128.3, 128.3	
C(1)–C(6)–Cl(1)	121.5, 121.7		C(7)–C(12)–Cl(2)	120.5, 120.6	
C(1)–C(6)–C(5)	122.3, 121.4		C(7)–C(12)–C(11)	121.9, 122.0	
C(5)–C(6)–Cl(1)	115.9, 116.4		C(11)–C(12)–Cl(2)	116.9, 116.8	
C(6)–C(5)–C(4)	120.1, 120.7		C(12)–C(11)–C(10)	119.5, 119.6	
C(5)–C(4)–C(3)	120.1, 120.2		C(11)–C(10)–C(9)	120.5, 120.7	
C(4)–C(3)–C(2)	119.5, 118.6		C(10)–C(9)–C(8)	118.9, 118.8	
C(3)–C(2)–C(1)	123.0, 123.6		C(9)–C(8)–C(7)	123.0, 122.8	
C(2)–C(1)–C(6)	114.2, 114.4		C(8)–C(7)–C(12)	114.4, 114.5	
C(1)–C(2)–N(1)	119.8, 119.8		C(7)–C(8)–N(2)	119.3, 119.6	
C(2)–N(1)–N(2)	120.2, 119.7		C(8)–N(2)–N(1)	119.8, 119.6	
N(2)–N(1)–O(1)	118.3, 118.3		N(1)–N(2)–O(2)	118.4, 118.4	
C(2)–N(1)–O(1)	121.1, 121.4		C(8)–N(2)–O(2)	120.8, 121.0	
C(2)–C(1)–C(7)	117.1, 117.5		C(8)–C(7)–C(1)	117.2, 117.1	

Cl(1)–C(6)–C(1)–C(7)	−13.1, −13.6	
C(6)–C(1)–C(7)–C(12)	−30.6, −32.6	
C(2)–C(1)–C(7)–C(8)	−23.0, −22.5	
C(2)–N(1)–N(2)–C(8)	−23.3, −24.9	
O(1)–N(1)–N(2)–O(2)	−4.9, −5.6	
C(7)–C(1)–C(2)–N(1)	6.9, 7.6	
C(1)–C(2)–N(1)–N(2)	16.6, 16.4	

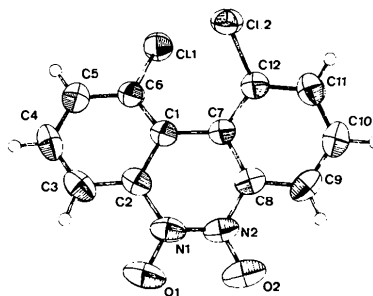|		
C(1)–C(7)–C(12)–Cl(2)	−20.6, −18.5
C(1)–C(7)–C(8)–N(2)	17.1, 14.8
C(7)–C(8)–N(2)–N(1)	6.1, 8.9

Fig. 1. View of the molecule showing atomic numbering and vibrational ellipsoids (50% probability level).

Discussion. If the two molecules in the asymmetric unit are chosen to have the same sense of chirality, they are related by a translation of approximately (0.50, 0.11, −0.15) together with a rotation of about 80° about an axis that nearly corresponds to the principal molecular axis with the largest moment of inertia. The two molecules differ by at most 0.013 (8) Å in bond length and 0.9 (6)° in bond angle. They closely resemble the 4,5-dimethyl analogue. Thus the same spiral pattern is formed by Cl(1)–C(6)–C(1)–C(7)–C(12)–Cl(2) to give Cl(1)···Cl(2) distances of 3.08 and 3.09 Å.

However, the approach to twofold rotational symmetry is not as close as in the dimethyl compound, and, in particular, the conformation of the diazine ring is less regular. The N—N bond distances are 1·329 (4) and 1·336 (4) Å; otherwise the dinitroso fragment is similar to that in other dinitroso compounds (Prout, Stothard & Watkin, 1978). There are no unusually short intermolecular contacts.

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Structure of 2-(2,6-Dimethoxyphenyl)-2,5-dimethylbicyclo[3.2.1]octane-6,8-dione

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Abstract. $C_{18}H_{22}O_4$, orthorhombic, $P2_12_12_1$, $a = 7·343$ (4), $b = 11·251$ (4), $c = 19·357$ (4) Å, $Z = 4$, $D_m = 1·20$, $D_c = 1·254$ g cm^{-3}, $F(000) = 648$, μ(Mo $K\alpha) = 0·94$ cm^{-1}. X-ray intensity data were collected on a Nonius CAD-4 diffractometer and the structure was solved by direct methods. Full-matrix least-squares refinement gave $R = 0·052$ ($R_w = 0·045$) for 1053 observed reflections. The stereochemical configuration at C(2) has been shown to be 2-*exo*-methyl-2-*endo*-(2,6-dimethoxyphenyl), *i.e.* (3) in contrast to the structure (2) assigned earlier based on its ^{1}H NMR data.

(1)   (2)   (3)
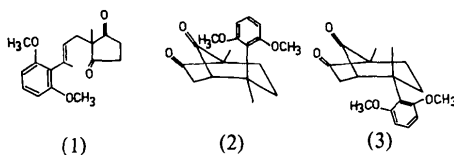
Introduction. X-ray crystallographic analysis of the title compound was undertaken to establish the stereochemistry of the substituents at C(2), the first step in obtaining an insight into the mechanism of its formation during the acid-catalysed cyclization of the diketone (1) (Kasturi, Madhava Reddy & Murthy, 1981). The puzzling fact was that this compound, assigned the 2-*exo*-aryl-2-*endo*-methyl configuration (2), based on the analogy of its ^{1}H NMR spectral characteristics with other similar compounds (Kasturi & Madhava Reddy, 1981) was, however, obtained as the only isomer of 2-(2,6-dimethoxyphenyl)-2,5-dimethylbicyclo[3.2.1]octane-6,8-dione.

Transparent needle-shaped crystals of (2) were obtained by slow evaporation from a solution of the racemate in benzene–hexane. The single crystals obtained were optically active and were found to belong to the orthorhombic space group $P2_12_12_1$. A crystal of dimensions 0·3 × 0·2 × 0·06 mm was used for collecting intensity data and a total of 1370 independent reflections were measured in the $\omega/2\theta$ scan mode using monochromated Mo $K\alpha$ ($\lambda = 0·7107$ Å) radiation. No correction was made for absorption. Out of 1370 reflections, 1053 were considered as observed ($|F_{obs}| \geq 2\sigma (|F_{obs}|)$).

The structure was solved by direct methods using the program *MULTAN* 80 (Main, 1980). Initial structure refinement was carried out by block-diagonal least-squares methods. The positions of the H atoms attached to the rigid C skeleton were determined from stereochemical considerations and those of the methyl group were located in a difference map and included in further refinements. The full-matrix refinement using the program *SHELX* (Sheldrick, 1976) treating C and O atoms anisotropically and H atoms isotropically with the weighting scheme $w = 1·28/[\sigma^2(|F_{obs}|) + 0·00035(|F_{obs}|)^2]$ led to the final R value of 0·052 ($R_w = 0·045$). Final positional parameters and temperature factors for non-H atoms are given in Table 1 and those of H atoms in Table 2.*

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36721 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.