

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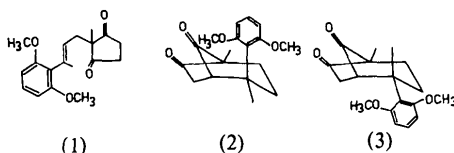
Structure of 2-(2,6-Dimethoxyphenyl)-2,5-dimethylbicyclo[3.2.1]octane-6,8-dione

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Abstract. C₁₈H₂₂O₄, orthorhombic, *P*2₁2₁2₁, *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* α) = 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 ¹H NMR data.



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 ¹H 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.

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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 *P*2₁2₁2₁. 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* α (λ = 0.7107 Å) radiation. No correction was made for absorption. Out of 1370 reflections, 1053 were considered as observed ($|F_{\text{obs}}| \geq 2\sigma(|F_{\text{obs}}|)$).

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 $w = 1.28/[\sigma^2(|F_{\text{obs}}|) + 0.00035(|F_{\text{obs}}|)^2]$ 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.*

* 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.

Table 1. Final positional coordinates ($\times 10^5$) and equivalent isotropic temperature factors for the non-H atoms with e.s.d.'s in parentheses

$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	U_{eq} (Å ²)
C(1)	64638 (71)	25551 (36)	13354 (23)	0.047 (2)
C(2)	56123 (63)	28992 (41)	20460 (22)	0.039 (1)
C(3)	52365 (92)	42554 (45)	19929 (28)	0.048 (2)
C(4)	43379 (100)	46503 (55)	13160 (30)	0.060 (2)
C(5)	52489 (88)	41700 (45)	6593 (26)	0.058 (2)
C(6)	72956 (97)	43613 (55)	7510 (27)	0.064 (2)
C(7)	80887 (85)	33388 (58)	11362 (31)	0.061 (2)
C(8)	51194 (80)	28666 (49)	7653 (26)	0.055 (2)
C(9)	38189 (81)	21918 (65)	21407 (38)	0.064 (2)
C(10)	68657 (64)	26277 (39)	26806 (22)	0.038 (2)
C(11)	83708 (67)	18543 (44)	26707 (23)	0.043 (2)
C(12)	94661 (75)	16915 (51)	32467 (28)	0.055 (2)
C(13)	90746 (81)	22568 (57)	38560 (29)	0.057 (2)
C(14)	75330 (79)	29478 (53)	39097 (27)	0.052 (2)
C(15)	64547 (68)	31097 (40)	33292 (24)	0.043 (2)
C(16)	98094 (111)	2284 (68)	20902 (41)	0.067 (3)
C(17)	42068 (137)	40514 (95)	40479 (35)	0.090 (3)
C(18)	44182 (203)	46454 (85)	-59 (43)	0.088 (4)
O(1)	80988 (76)	52283 (46)	5461 (21)	0.095 (2)
O(2)	41270 (73)	21768 (37)	4703 (20)	0.086 (2)
O(3)	87110 (58)	12398 (41)	20742 (19)	0.079 (2)
O(4)	48590 (53)	37432 (34)	33846 (16)	0.063 (1)

Table 2. Final positional coordinates ($\times 10^3$) and isotropic temperature factors ($\times 10^2$) for the H atoms with e.s.d.'s in parentheses

The temperature factor is of the form: $T = \exp(-8\pi^2 U \sin^2\theta/\lambda^2)$.

	Bonded to	x	y	z	U (Å ²)
H(1)	C(1)	679 (6)	178 (4)	129 (2)	4.2 (1.2)
H(2)	C(3)	633 (7)	477 (5)	214 (3)	5.4 (1.5)
H(3)	C(3)	470 (6)	449 (4)	235 (2)	2.1 (1.2)
H(4)	C(4)	436 (8)	550 (6)	134 (3)	7.6 (1.8)
H(5)	C(4)	308 (9)	437 (5)	132 (3)	7.6 (2.0)
H(6)	C(7)	893 (9)	291 (6)	83 (3)	9.0 (2.1)
H(7)	C(7)	876 (7)	359 (4)	156 (3)	6.2 (1.5)
H(8)	C(9)	417 (7)	123 (6)	212 (3)	7.0 (1.6)
H(9)	C(9)	339 (9)	223 (6)	257 (3)	8.5 (2.3)
H(10)	C(9)	294 (9)	255 (5)	185 (3)	7.4 (1.9)
H(11)	C(12)	1046 (9)	112 (5)	320 (3)	6.8 (1.7)
H(12)	C(13)	975 (8)	219 (5)	420 (3)	7.3 (1.9)
H(13)	C(14)	732 (8)	336 (5)	434 (3)	7.7 (1.9)
H(14)	C(16)	938 (8)	-40 (6)	239 (3)	6.7 (2.0)
H(15)	C(16)	957 (9)	-21 (6)	166 (4)	8.7 (2.0)
H(16)	C(16)	1093 (11)	39 (6)	222 (4)	9.3 (2.6)
H(17)	C(17)	417 (8)	337 (5)	435 (3)	5.8 (1.7)
H(18)	C(17)	501 (11)	468 (6)	429 (4)	11.2 (2.9)
H(19)	C(17)	288 (12)	436 (7)	392 (4)	11.9 (2.8)
H(20)	C(18)	451 (13)	553 (9)	-5 (4)	13.4 (3.1)
H(21)	C(18)	345 (11)	477 (9)	9 (5)	11.1 (4.5)
H(22)	C(18)	514 (8)	428 (5)	-39 (4)	7.7 (2.0)

Discussion. A perspective view of the molecule viewed along the a axis is shown in Fig. 1. The methyl group at C(2) and the bridge-keto group are *syn* with respect to each other establishing the 2-*exo*-methyl-

2-*endo*-(2,6-dimethoxyphenyl) configuration (3) in contrast to the earlier structure (2). The bond lengths and bond angles involving non-H atoms in structure (3) are recorded in Figs. 2(a) and 2(b) respectively. The C(sp^3)-C(sp^3) bond distances vary from 1.522 (9)-1.560 (6) Å and those of C(sp^3)-C(sp^2) from 1.484 (8)-1.565 (6) Å and can be explained in terms of the number of C and H substitutions at the C atoms involved. However, the shorter length of the C(5)-C(8) bond [1.484 (8) Å] compared to C(1)-C(8) [1.521 (7) Å] remains unexplained. The bond lengths and angles in this structure are comparable, within the limits of experimental error, with those of 2-*exo*-methyl-2-*endo*-(2-methoxyphenyl)-5-methylbicyclo[3.2.1]octane-6,8-dione (Kasturi, Murthy, Madhava Reddy, Bhadbhade & Venkatesan, 1981). The torsion angles (Fig. 3) within the rings show that the five-, six- and seven-membered rings of the bicyclo-octane moiety are in distorted envelope, chair and boat conformations respectively as observed in

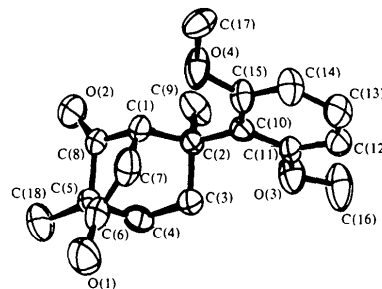


Fig. 1. Perspective view down the a axis, of the molecule.

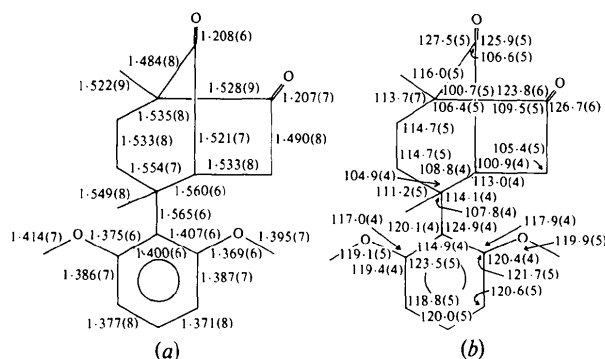


Fig. 2. (a) Bond lengths (Å) and (b) bond angles (°) involving non-H atoms.

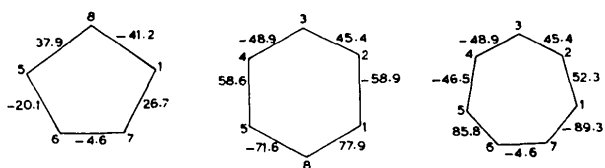


Fig. 3. Endocyclic torsion angles of the bicyclo-octane moiety (standard deviations are $< 1^\circ$).

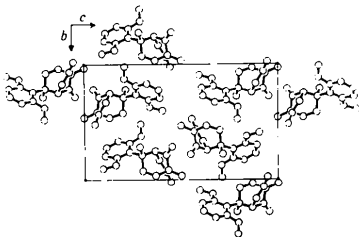


Fig. 4. Packing of the molecules viewed down the *a* axis.

many natural products containing this skeleton (e.g. Coggon & Sim, 1969). The angular deformations of the phenyl ring caused by the substituents are in keeping with the pattern expected for substituted benzenes (Domenicano, Vaciago & Coulson, 1975). The intramolecular overcrowding of the *ortho* substituents of the phenyl ring is minimized by out-of-plane displacement of the substituents.

The angle between the least-squares planes passing through the phenyl-ring atoms and that of the plane through the atoms C(9), C(10), C(2) and C(5) is 106.6 (5)°. In 1-arylcyclohexane derivatives, the conformation of minimum steric interaction between the aryl and cyclohexane ring atoms is the one where the rings are orthogonal to each other (Allinger, Allinger, Darooge & Greenberg, 1962). Thus, the conformation of the aryl group in structure (3) appears to correspond to the most stable one and the disposition of the bridgehead and the keto-methylene protons with

respect to the plane of the aryl ring could perhaps be used to examine the magnetic anisotropy effects of the aryl ring on these protons.

The molecular packing viewed down the *a* axis is shown in Fig. 4. There are no short contacts within 3.5 Å.

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Ethyl (Z)-2-Nitro-3-(4-nitrophenyl)acrylate

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Abstract. C₁₁H₁₀N₂O₆, *M_r* = 266.1, triclinic, *P* $\bar{1}$, *a* = 7.803 (4), *b* = 7.860 (5), *c* = 10.961 (5) Å, α = 77.19 (4), β = 82.16 (4), γ = 68.89 (5)°, *U* = 610.35 Å³, *Z* = 2, *D_c* = 1.45 Mg m⁻³, μ = 0.13 mm⁻¹

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(Mo *K* α radiation), *R* = 0.049 for 1558 observed reflections. The two olefinic C atoms and the attached N and carbonyl group all lie in one plane, to which the olefinic nitro group and benzene ring make angles of 80.5 (5) and 9.3 (5)° respectively. The aromatic nitro group is twisted out of the plane of the benzene ring by 20.2 (4)°.