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Bicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxamide, $C_9H_{10}N_2O_2$

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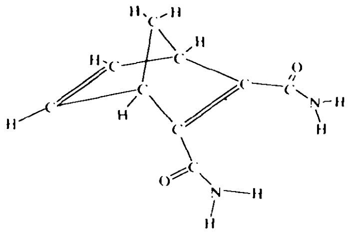
Abstract

Intramolecular hydrogen bonding between the amido groups [O(81)···H(111) = 1.89 (4) Å and N(11)—H(111)···O(81) = 151 (3)°] maintains the molecule in a conformation that favours partial delocalization between the amido groups and the adjacent C(2)=C(7) double bond. This can be inferred from a shortening of the C(1)—C(2) and C(7)—C(8) single bonds [1.479 (3) and 1.481 (3) Å, respectively] and a small lengthening of the C(2)=C(7) double bond [1.341 (3) Å]. Partial relief of the strain in the cycle then allows a shortening of the C(4)=C(5) double bond [1.285 (4) Å] [1.330 (3) Å in unsubstituted norbornadiene; Morino, Kuchitsu & Yokoseki (1967). *Bull. Chem. Soc. Jpn*, **40**, 1552]. The crystal also exhibits intermolecular N—H···O hydrogen bonding, with N···O distances in the range 2.960 (3)-2.978 (3) Å and N—H···O angles between 160 (3) and 174 (3)°.

Comment

The crystal structure of the title compound (I) was determined in order to elucidate the intramolecular hydrogen bonding in the course of a study of the electron-transfer properties of norbornadiene derivatives.



(I)

The solution NMR spectrum {DMSO-d_6, 1.99, 1.84 [2, *AB* quartet, *J* = 7 Hz, H(92) and H(91)], 3.98 [2, *s*, H(31) and H(61)], 6.90 [2, *s*, H(41), H(51)], 7.51, 8.68 [2 and 2, *s*, H(111), H(112), H(811) and H(812)] p.p.m.} presents two unexpected features: an *AB* quartet for the CH_2 protons, due to the long distance effect of the carboxamide groups, and two single peaks for the four NH_2 protons, which indicates that the intramolecular hydrogen bonding is maintained in solution. However, the rotation around the C—N bonds is very fast on the NMR time scale, which leads to two sharp peaks with the same integration.

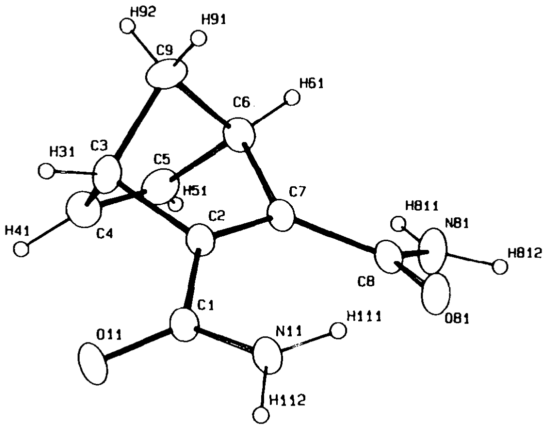


Fig. 1. View of $C_9H_{10}N_2O_2$ showing the atom-numbering scheme. Thermal ellipsoids are shown at 20% probability levels; H atoms are drawn with an artificial *B* of 1.0 Å^2 for clarity.

Experimental

The compound was prepared by a procedure described in the literature (Diels & Alder, 1931; Taniguchi, Ykeda, Yoshida & Imoto, 1977). The compound was crystallized from methanol solution.

Crystal data

$C_9H_{10}N_2O_2$
M_r = 178.191
Monoclinic
$P2_1/c$
a = 5.984 (2) Å
b = 11.703 (4) Å
c = 12.559 (4) Å
β = 99.11 (2)°
V = 868 (3) Å^3
Z = 4

D_x = 1.363 Mg m^{-3}
Mo $K\alpha$ radiation
λ = 0.71069 Å
Cell parameters from 25 reflections
θ = 12-13°
μ = 0.0921 mm^{-1}
T = 297 K
Prism
0.32 × 0.27 × 0.10 mm
Colourless

Data collection

Enraf-Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: none
1738 measured reflections
1552 independent reflections
1060 observed reflections [$I > 3\sigma(I)$]

$R_{\rm int}$ = 0.017
$\theta_{\rm max}$ = 25°
$h = -7 \rightarrow 7$
$k = 0 \rightarrow 13$
$l = 0 \rightarrow 14$
3 standard reflections
frequency: 60 min
intensity variation: none

Refinement

Refinement on F
R = 0.040

$\Delta\rho_{\rm max}$ = 0.19 e Å^{-3}
$\Delta\rho_{\rm min}$ = −0.163 e Å^{-3}

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$wR = 0.039$
1060 reflections
149 parameters
Only coordinates of H atoms refined
Unit weights applied
$(\Delta/\sigma)_{\max} = 0.001$
Extinction correction: Gaussian (Zachariasen, 1968)
Extinction coefficient: 75 (7)
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.3.1)

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

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
C(1)	0.7854 (4)	0.0713 (2)	0.0988 (2)	0.0347
C(2)	0.6530 (4)	0.1314 (2)	0.1716 (2)	0.0343
C(3)	0.4618 (5)	0.2134 (3)	0.1247 (2)	0.0431
C(4)	0.5457 (6)	0.3331 (3)	0.1530 (3)	0.0541
C(5)	0.5708 (5)	0.3439 (3)	0.2560 (3)	0.0514
C(6)	0.5038 (5)	0.2322 (2)	0.3019 (2)	0.0423
C(7)	0.6795 (4)	0.1423 (2)	0.2792 (2)	0.0347
C(8)	0.8442 (5)	0.0882 (2)	0.3648 (2)	0.0375
C(9)	0.3082 (5)	0.1987 (3)	0.2118 (3)	0.0510
N(11)	0.8857 (4)	−0.0262 (2)	0.1312 (2)	0.0386
O(11)	0.7947 (3)	0.1135 (2)	0.0089 (1)	0.0440
N(81)	0.8950 (5)	0.1472 (2)	0.4558 (2)	0.0470
O(81)	0.9266 (3)	−0.0070 (2)	0.3534 (1)	0.0425

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

C(1)—C(2)	1.479 (3)	C(6)—C(7)	1.545 (4)
C(1)—N(11)	1.323 (3)	C(6)—C(9)	1.544 (4)
C(1)—O(11)	1.241 (3)	C(7)—C(8)	1.481 (3)
C(2)—C(3)	1.538 (4)	C(8)—N(81)	1.329 (3)
C(2)—C(7)	1.341 (3)	C(8)—O(81)	1.236 (3)
C(3)—C(4)	1.511 (4)	N(11)···O(81)	2.772(3)
C(4)—C(5)	1.285 (4)	O(81)···H(111)	1.89 (4)
C(5)—C(6)	1.509 (4)		
N(11)—C(1)—C(2)	118.7 (2)	C(7)—C(6)—C(5)	106.8 (2)
O(11)—C(1)—C(2)	118.6 (2)	C(9)—C(6)—C(5)	99.0 (2)
O(11)—C(1)—N(11)	122.7 (2)	C(9)—C(6)—C(7)	98.7 (2)
C(3)—C(2)—C(1)	119.9 (2)	C(6)—C(7)—C(2)	106.0 (2)
C(7)—C(2)—C(1)	132.8 (2)	C(8)—C(7)—C(2)	130.5 (2)
C(7)—C(2)—C(3)	106.7 (2)	C(8)—C(7)—C(6)	123.4 (2)
C(4)—C(3)—C(2)	106.8 (2)	N(81)—C(8)—C(7)	116.0 (2)
C(9)—C(3)—C(2)	98.6 (2)	O(81)—C(8)—C(7)	122.3 (2)
C(9)—C(3)—C(4)	98.6 (2)	O(81)—C(8)—N(81)	121.7 (2)
C(5)—C(4)—C(3)	108.0 (3)	C(6)—C(9)—C(3)	91.3 (2)
C(6)—C(5)—C(4)	107.6 (3)	N(11)—H(111)···O(81)	151 (3)

Data collection: *CAD*-4 *Software* (Enraf-Nonius, 1989). Cell refinement: *CAD*-4 *Software CELDIM*. Data reduction: *CRYSTALS RC*85 (Watkin, Carruthers & Betteridge, 1985). Program(s) used to solve structure: *CRYSTALS*; *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *CRYSTALS*. Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *CRYSTALS*.

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 71686 (12 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: PA1037]

References

Diels, O. & Alder, K. (1931). *Ann. Chem.* **490**, 236-241.
Enraf-Nonius (1989). *CAD*-4 *Software*. Version 5.0. Enraf-Nonius, Delft, The Netherlands.
Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Morino, Y., Kuchitsu, K. & Yokoseki, A. (1967). *Bull. Chem. Soc. Jpn*, **40**, 1552.
Sheldrick, G. M. (1985). *SHELXS*86. *Program for the Solution of Crystal Structures*. Univ. of Göttingen, Germany.
Taniguchi, H., Ykeda, T., Yoshida, Y. & Imoto, E. (1977). *Bull. Chem. Soc. Jpn*, **50**, 2694-2699.
Watkin, D. J., Carruthers, J. R. & Betteridge, P. W. (1985). *CRYSTALS. An Advanced Crystallographic Computer Program*. Chemical Crystallographic Laboratory, Univ. of Oxford, England.
Zachariasen, W. H. (1968). *Acta Cryst.* A**24**, 212-216.

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Dimethyl 9-Phenyl-1,4-dihydro-1,4-ethenoanthracene-11,12-dicarboxylate

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Abstract

The molecule $C_{26}H_{20}O_4$ has normal geometry and dimensions. The methoxycarbonyl group that is remote from the phenyl substituent is conjugated with the C11=C12 double bond [C=C—C=O torsion angle = −163.2 (4)°, cos^2(angle) = 0.92], while the adjacent group is only very slightly conjugated [C=C—C=O torsion angle = 68.1 (5)°, cos^2(angle) = 0.14].

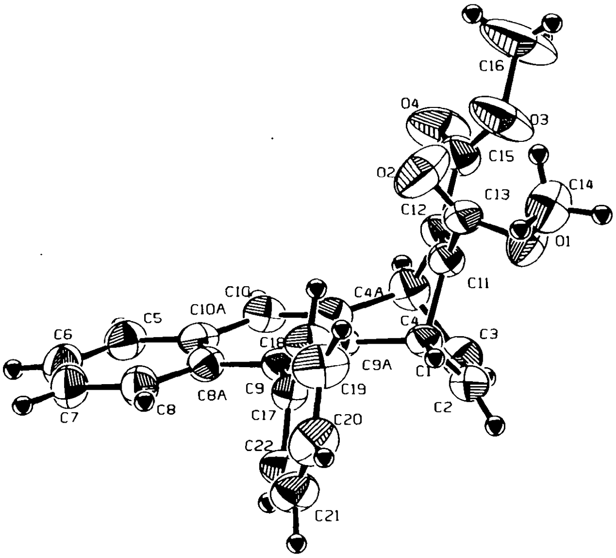

Fig. 1. View of the molecule with 50% probability ellipsoids.

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