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1,3-Bis(2,5-dihydro-5,5-dimethyl-2-oxo-1-pyrrolyl)-2,2-dimethyl-1,3-propanedione

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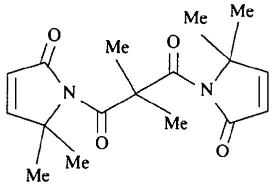
Abstract

The title compound, $C_{17}H_{22}N_2O_4$, is a linked bischromophore. An X-ray structure determination confirmed the restricted rotation of the alicyclic chain segment as suggested by ^1H NMR spectroscopic results in solution.

Comment

The photochemical behavior of 2,5-dihydro-5,5-dimethylpyrrole-2-one (Ihlefeld & Margaretha, 1992) parallels that of the pyrimidine bases in DNA, *e.g.* uracil or thymine. We have synthesized a series of 1,1′-linked bischromophores with different spacers. In order to characterize one of the resulting products unambiguously, an X-ray structure determination of the title compound, (I), was undertaken.



(I)

The title compound can be considered to be a derivative of 2,2-dimethylmalonic acid, where the carboxy groups are replaced by semicyclic imide systems. Both of these systems exhibit an *E* configuration (O41—C31—N51—C61—O71 and O42—C32—N52—C62—O72). In this sterically favored arrangement, the imide O atoms (O41···O71 and O42···O72) are at a maximum distance from one another. The spatial vicinity of both almost planar imide systems causes a strong steric interaction between the O71 and O72 atoms, which is reduced by a considerable distortion of the bond angle at the central C10 atom. While the C21—C10—C22 angle of 109.1 (1)° almost corresponds to that of an sp^3-hybridized C atom, the C31—C10—C32 bond angle of 123.2 (1)° is considerably enlarged.

As expected, both five-membered rings are almost flat [maximum deviation of 0.03 (2) Å in the N52—C62—C82—C92—C102 ring]. Even the least-squares planes through each of the eight-atom sets O71, N51, C61, C81, C91, C101, C31, O41 and O72, N52, C62, C82, C92, C102, C32, O42, show a maximum deviation of only −0.075 (7) Å (*PLATON*92; Spek, 1992).

The ^1H NMR spectrum of the title compound is remarkable as it shows two pairs of methyl proton signals for the *a priori* four equivalent methyl groups on the two heterocyclic rings. Indeed, the crystal structure suggests that the two ring carbonyl O atoms (O71 and O72) collide on rotation of the open-chain N—C(=O)—C—C(=O)—N segment and, therefore, the two pairs of methyl groups become diastereotopic.

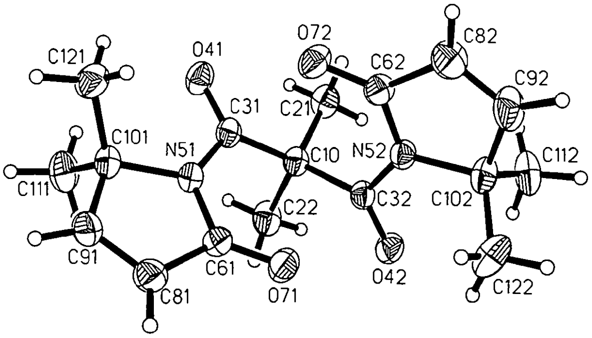


Fig. 1. *ORTEP*II drawing (Johnson, 1976), as implemented in *SHELXTL-Plus* (Sheldrick, 1992), of the title compound showing displacement ellipsoids at 30% probability and the atomic numbering scheme.

Experimental

The title compound results in 58% yield from the reaction of two moles of 2,5-dihydro-5,5-dimethylpyrrole-2-one and one mole of dimethylmalonic acid dichloride (Wrobel, 1994). ^1H NMR (400 MHz, $CDCl_3$): δ 1.51 (*s*, 6H), 1.55 (*s*, 6H), 1.65 (*s*, 6H), 5.86 (*d*, J = 6.1 Hz, 2H), 7.09 p.p.m. (*d*, J = 6.1 Hz, 2H). Suitable single crystals (m.p. 401–402 K) were obtained from an ethoxyethane solution.

Crystal data

$C_{17}H_{22}N_2O_4$	Cu $K\alpha$ radiation
M_r = 318.37	λ = 1.54178 Å

Monoclinic
$P2_1/n$
$a = 10.882\ (1)$ Å
$b = 10.367\ (1)$ Å
$c = 15.778\ (1)$ Å
$\beta = 99.39\ (1)°$
$V = 1756.1\ (3)$ Å^3
$Z = 4$
$D_x = 1.204$ Mg m^{-3}
D_m not measured

Cell parameters from 24 reflections
$\theta = 42.5–49.8°$
$\mu = 0.707$ mm^{-1}
$T = 293\ (1)$ K
Transparent prism
$0.5 \times 0.4 \times 0.3$ mm
Colorless

Data collection

Enraf–Nonius CAD-4 diffractometer
$2\theta/\omega$ scans
Absorption correction: none
3624 measured reflections
3386 independent reflections
3213 observed reflections $[I > 2\sigma(I)]$

$R_{\rm int} = 0.014$
$\theta_{\rm max} = 76.5°$
$h = 0 \rightarrow 13$
$k = 0 \rightarrow 12$
$l = -19 \rightarrow 19$
3 standard reflections frequency: 120 min intensity decay: 1%

Refinement

Refinement on F^2
$R(F) = 0.0437$
$wR(F^2) = 0.1334$
$S = 1.115$
3382 reflections
237 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0654P)^2 + 0.4297P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.103$
$\Delta\rho_{\rm max} = 0.234$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.152$ e Å^{-3}

Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0061 (5)
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

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	$U_{\rm eq}$
C10	1.0991 (1)	0.1344 (2)	0.2328 (1)	0.0431 (3)
C21	1.0913 (2)	0.2822 (2)	0.2307 (1)	0.0570 (4)
C31	0.9657 (1)	0.0795 (2)	0.2130 (1)	0.0427 (3)
O41	0.8824 (1)	0.1473 (1)	0.1774 (1)	0.0552 (3)
N51	0.9445 (1)	−0.0526 (1)	0.2187 (1)	0.0423 (3)
C61	1.0203 (1)	−0.1452 (2)	0.2657 (1)	0.0461 (3)
O71	1.1178 (1)	−0.1245 (1)	0.3130 (1)	0.0602 (3)
C81	0.9578 (2)	−0.2689 (2)	0.2479 (1)	0.0579 (4)
C91	0.8499 (2)	−0.2507 (2)	0.1978 (1)	0.0578 (4)
C101	0.8275 (1)	−0.1127 (2)	0.1734 (1)	0.0481 (4)
C111	0.8172 (2)	−0.0979 (2)	0.0761 (1)	0.0727 (6)
C121	0.7122 (2)	−0.0636 (2)	0.2055 (1)	0.0641 (5)
C22	1.1607 (2)	0.0874 (2)	0.1570 (1)	0.0624 (5)
C32	1.1900 (1)	0.1032 (2)	0.3158 (1)	0.0421 (3)
O42	1.2979 (1)	0.0805 (1)	0.3126 (1)	0.0553 (3)
N52	1.1554 (1)	0.1268 (1)	0.3961 (1)	0.0437 (3)
C62	1.0365 (1)	0.1437 (2)	0.4151 (1)	0.0478 (4)
O72	0.9396 (1)	0.1349 (1)	0.3650 (1)	0.0598 (3)
C82	1.0524 (2)	0.1745 (2)	0.5073 (1)	0.0668 (5)
C92	1.1712 (2)	0.1721 (2)	0.5397 (1)	0.0709 (5)
C102	1.2514 (2)	0.1357 (2)	0.4750 (1)	0.0552 (4)
C112	1.3472 (2)	0.2401 (2)	0.4672 (1)	0.0753 (6)
C122	1.3122 (2)	0.0053 (2)	0.4980 (2)	0.0805 (6)

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

C10—C21	1.535 (2)	C101—C121	1.517 (2)
C10—C32	1.541 (2)	C101—C111	1.528 (2)
C10—C22	1.543 (2)	C32—O42	1.206 (2)
C10—C31	1.542 (2)	C32—N52	1.402 (2)
C31—O41	1.210 (2)	N52—C62	1.385 (2)
C31—N51	1.394 (2)	N52—C102	1.493 (2)
N51—C61	1.398 (2)	C62—O72	1.213 (2)
N51—C101	1.491 (2)	C62—C82	1.472 (2)
C61—O71	1.212 (2)	C82—C92	1.311 (3)
C61—C81	1.457 (2)	C92—C102	1.495 (3)
C81—C91	1.318 (2)	C102—C122	1.523 (3)
C91—C101	1.491 (3)	C102—C112	1.521 (3)
C21—C10—C32	104.72 (12)	N51—C101—C111	110.88 (13)
C21—C10—C22	109.09 (14)	C91—C101—C111	109.74 (15)
C32—C10—C22	106.99 (12)	C121—C101—C111	111.9 (2)
C21—C10—C31	108.46 (12)	O42—C32—N52	118.63 (13)
C32—C10—C31	123.19 (12)	O42—C32—C10	120.02 (13)
C22—C10—C31	103.91 (12)	N52—C32—C10	120.05 (12)
O41—C31—N51	118.70 (13)	C62—N52—C32	128.06 (12)
O41—C31—C10	119.26 (13)	C62—N52—C102	111.28 (12)
N51—C31—C10	120.64 (12)	C32—N52—C102	120.66 (12)
C31—N51—C61	128.25 (12)	O72—C62—N52	126.33 (13)
C31—N51—C101	121.19 (12)	O72—C62—C82	127.50 (15)
C61—N51—C101	110.54 (12)	N52—C62—C82	106.17 (13)
O71—C61—N51	125.90 (15)	C92—C82—C62	109.3 (2)
O71—C61—C81	127.48 (15)	C82—C92—C102	112.79 (15)
N51—C61—C81	106.61 (13)	N52—C102—C92	100.23 (13)
C91—C81—C61	109.4 (2)	N52—C102—C122	111.21 (15)
C81—C91—C101	112.54 (15)	C92—C102—C122	109.9 (2)
N51—C101—C91	100.80 (12)	N52—C102—C112	111.83 (14)
N51—C101—C121	112.81 (13)	C92—C102—C112	111.1 (2)
C91—C101—C121	110.19 (14)	C122—C102—C112	112.0 (2)

The systematic absences ($h0l$: $h + l = 2n$ and $0k0$: $k = 2n$) indicate $P2_1/n$ as the only possible space group. All H atoms were refined with distance restraints for the C—H distances.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *CADSHEL* (Kopf, 1987). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL-Plus* (Sheldrick, 1992). Software used to prepare material for publication: *CIF2TEX* (Kopf, 1992*a*) and *FCF2FOC* (Kopf, 1992*b*).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AB1302). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Methyl *trans*-9,10-Dihydro-9,10-ethanoanthracene-11-carboxylate

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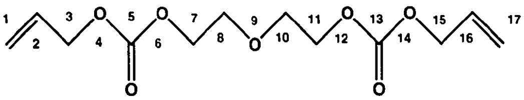
Abstract

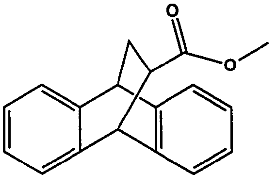
The title compound, $C_{18}H_{16}O_2$, was prepared as an important intermediate in the preparation of deuterium-labelled diethylene glycol bis(allyl carbonate). The bond lengths and angles are similar to those reported for *trans*-9,10-dihydro-9,10-ethanoanthracene-11-carboxylic acid.

Comment

Recent studies of the free radical polymerization of diethylene glycol bis(allyl carbonate), (1), have shown that hydrogen abstraction from position 8 is kinetically favoured, but the thermodynamic product is that derived from allylic abstraction (Qureshi, Solomon & Kelly, 1995; Qureshi, Schiesser & Solomon, 1995). Intramolecular hydrogen transfer from the allylic position 3 to position 8 would explain the formation of the allylic radicals. To test this hypothesis, compound (1), deuterium-labelled at positions 3 and 15, was synthesized. An important intermediate in this preparation was methyl *trans*-9,10-dihydro-9,10-ethanoanthracene-11-carboxylate, (2), which was prepared following the method of Wawzonek & Hallum (1953). While the ^{13}C NMR spectrum could be assigned in accordance with the structure, the aromatic protons in the ^1H NMR spectrum could not. An X-ray structural analysis of (2) was carried out in order to confirm the identity of this compound.



(1)



(2)

The bond lengths and angles found for compound (2) are similar to those found for the corresponding carboxylic acid, *trans*-9,10-dihydro-9,10-ethanoanthracene-11-carboxylic acid (Csoregh, Czugler, Ertan, Weber & Ahrendt, 1990), which crystallizes as a clathrate with dimethyl sulfoxide. Also, the orientation of the carboxylate group, with a torsion angle C(12)—C(11)—C(13)—O(1) of 10.4 (2)°, is similar to that observed for the carboxylic acid group, where the corresponding torsion angle is −5.0°.

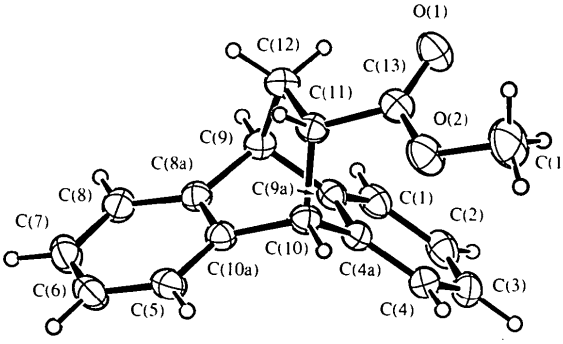


Fig. 1. An *ORTEP*II drawing (Johnson, 1976) of compound (2). Displacement ellipsoids are drawn at the 50% probability level.

Experimental

Crystals of the title compound were obtained from light petroleum.

Crystal data

$C_{18}H_{16}O_2$
M_r = 264.31
Monoclinic
$P2_1/n$
a = 13.1844 (9) Å
b = 6.2358 (7) Å
c = 17.562 (2) Å
β = 107.719 (6)°

Cu $K\alpha$ (Ni-filtered) radiation
λ = 1.5418 Å
Cell parameters from 25 reflections
θ = 21.6–40.6°
μ = 0.650 mm^{-1}
T = 293 (1) K

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