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1,3-Diphenyl-2-tricyclo[3.3.1.1^{3,7}]dec-2-ylidenepropane-1,3-diimine, and its -1-imino-3-one and -1,3-dione Derivatives

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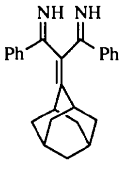
Abstract

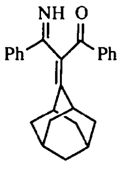
1,3-Diphenyl-2-tricyclo[3.3.1.1^{3,7}]dec-2-ylidenepropane-1,3-diimine, $C_{25}H_{26}N_2$, (1), 1-imino-1,3-diphenyl-2-tricyclo[3.3.1.1^{3,7}]dec-2-ylidenepropan-3-one, $C_{25}H_{25}NO$, (2) and 1,3-diphenyl-2-tricyclo[3.3.1.1^{3,7}]dec-2-ylidenepropane-1,3-dione, $C_{25}H_{24}O_2$, (3), were prepared from the reactions of 2-(dicyanomethylene)adamantane with phenylmagnesium bromide upon workup with dry methanol or dilute acid aqueous solution, and their crystal structures were determined by X-ray diffraction. Compounds (1) and (2) have similar molecular structures with the two imino groups in (1) and the imino and ketone groups in (2) being on the same side of the C1, C2, C12, C13 plane, compared with the two O atoms in compound (3), which are on opposite sides.

Comment

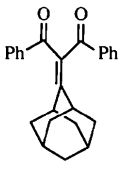
Michael addition reactions involve organometallic compounds with activated double bonds. Grignard reagents reacting with ylidenemononitriles always generate 1,4-addition or reductive products (Latif, Mishriky & Mohsen, 1974; Latif, Zeid & Assad, 1970). The nature of the resulting products depends on the organomagnesium halides as well as on the substrate, in particular on the stereochemical requirements of each (Latif, Girgis & Michael, 1970). Here, we report on the reactions of 2-(dicyanomethylene)adamantane with phenylmagnesium bromide which generate 1,2-addition products. The generation of different 1,2-products instead of 1,4-products or reductive products is ascribed to the steric effects between 2-(dicyanomethylene)adamantane and phenylmagnesium bromide.



(1)



(2)



(3)

The crystals of the title compounds, (1), (2) and (3), all have centrosymmetric monoclinic space groups and have similar cell volumes. However, compound (3) belongs to a *C*-centered rather than a primitive space group like those of (1) and (2). Compounds (1) and (2) have similar molecular structures with the two imino groups in (1) and the imino and ketone groups in (2) all on the same side of the C1, C2, C12, C13 plane around C1. There is a crystallographic twofold axis through C1, C2 and C6 in (3), and the two O atoms are on opposite sides of the C1, C2, C12, C13 plane. The C═NH bond length [1.243 (3) Å] in (2) is shorter than those in (1) [1.269 (5) and 1.279 (5) Å] and the C═O bond length [1.239 (3) Å] in (2) is longer than those in (3) [1.224 (3) Å]. Compounds (1) and (2) have intramolecular hydrogen bonding *via* N1···HN2 and O···HN contacts [N1···N2 3.308 (5), N1···HN2 2.554 (3) Å; N···O 3.100 (3), O···HN 2.435 (2) Å]. The torsion angles C2—C1—C12—N1 and C2—C1—C13—N2 are 78.4 (3) and −131.9 (4)°, respectively, in (1), C2—C1—C12—O and C2—C1—C13—N are 89.2 (2) and −124.5 (3)°, respectively, in (2), and C2—C1—C8—O

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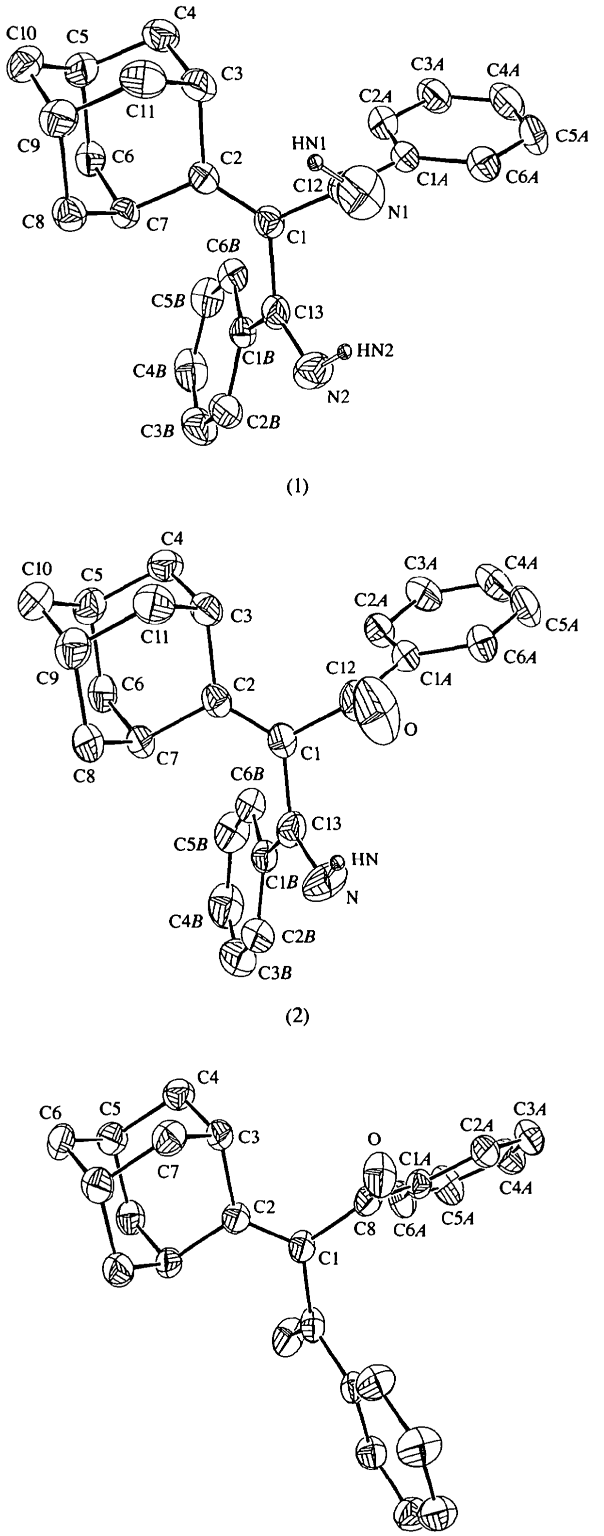

(1)

(2)

(3)

Fig. 1. *ORTEP* drawing (Johnson, 1965) of the molecular structure of (1), (2), and (3). Displacement ellipsoids are shown at the 30% probability level.

is 57.1 (2)° in (3). The ranges of all the C—C bond lengths in the title compounds are reasonable and none have any intermolecular contacts of structural significance.

Experimental

Compounds (1), (2) and (3) were synthesized as follows. A solution of 2-(dicyanomethylene)adamantane (4 mmol in thf) was added dropwise at room temperature to a thf solution of phenylmagnesium bromide (40 mmol, prepared from 40 mmol Mg and 40 mmol bromobenzene). A vigorous reaction occurred upon each addition. The mixture was then stirred at room temperature for 30 min and 40 mmol of dry methanol was added rapidly to the solution. This was removed under reduced pressure and the oily mixture was purified by flash column chromatography to obtain compound (1) (85%). The solid was recrystallized from hexane–ethyl acetate to give the pure pale-yellow crystals (m.p. 421–428 K) Analysis found: C 84.70, H 7.44, N 7.82%; calculated: C 84.70, H 7.39, N 7.90%. Compound (1) was poured into a dilute acid aqueous solution then extracted with dichloromethane to obtain a yield of 50% compound (2) and 10% compound (3). Both compounds were recrystallized from hexane–ethyl acetate after separation by flash column chromatography. Analysis of the pale-yellow crystals of (2) (m.p. 428–429 K) gave C 84.24, H 7.05, N 4.00%; calculated: C 84.47, H 7.09, N 3.94%. Crystals of (3) (m.p. 395–396 K) were colorless. Analysis found: C 83.82, H 6.66%; calculated: C 84.24, H 6.79%.

Compound (1)

Crystal data

$C_{25}H_{26}N_2$
$M_r = 354.49$
Monoclinic
$P2_1/c$
$a = 10.161\ (2)$ Å
$b = 15.585\ (3)$ Å
$c = 12.519\ (3)$ Å
$\beta = 103.95\ (2)°$
$V = 1924.1\ (7)$ Å^3
$Z = 4$
$D_x = 1.224$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 20.6–28.0°$
$\mu = 0.07$ mm^{-1}
$T = 298$ K
Tetragonal
0.50 × 0.50 × 0.45 mm
Pale yellow

Data collection

CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical ψ scan (North, Phillips & Mathews, 1968)
$T_{\min} = 0.926$, $T_{\max} = 0.996$
2646 measured reflections
2510 independent reflections

1829 reflections with $I > 2.5\sigma(I)$
$R_{\rm int} = 0.0094$
$\theta_{\max} = 22.5°$
$h = -10 \rightarrow 10$
$k = 0 \rightarrow 16$
$l = 0 \rightarrow 13$
3 standard reflections
frequency: 120 min
intensity decay: 3%

Refinement

Refinement on F
$R = 0.047$
$wR = 0.041$

$(\Delta/\sigma)_{\max} = 0$
$\Delta\rho_{\max} = 0.240$ e Å^{-3}
$\Delta\rho_{\min} = -0.190$ e Å^{-3}

$S = 4.03$
1829 reflections
245 parameters
H atoms calcutated, except those in N—H which were found from a ΔF map, and not refined
$w = 1/\sigma^2(F)$

Extinction correction: secondary
Extinction coefficient: 0.386406
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 1. *Selected geometric parameters (Å, °) for (1)*

N1—C12	1.269 (5)	C1—C12	1.510 (5)
N1—HN2	2.554 (4)	C1—C13	1.511 (5)
N2—C13	1.279 (5)	C2—C3	1.527 (5)
C1—C2	1.329 (5)	C2—C7	1.514 (4)
C2—C1—C12	121.9 (3)	C1—C2—C7	125.2 (3)
C2—C1—C13	125.1 (3)	N1—C12—C1	120.5 (3)
C12—C1—C13	112.5 (3)	N2—C13—C1	122.0 (3)
C1—C2—C3	123.0 (3)		
C2—C1—C12—N1	78.4 (3)	C2—C1—C13—N2	−131.9 (4)
C13—C1—C12—N1	−93.9 (3)	C12—C1—C13—N2	40.1 (2)

Compound (2)

Crystal data

$C_{25}H_{25}NO$
$M_r = 355.48$
Monoclinic
$P2_1/c$
$a = 10.196$ (1) Å
$b = 15.478$ (1) Å
$c = 12.664$ (3) Å
$\beta = 106.36$ (1)°
$V = 1917.7$ (5) Å^3
$Z = 4$
$D_x = 1.231$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 20.9$–$26.9°$
$\mu = 0.07$ mm^{-1}
$T = 298$ K
Tetragonal
0.30 × 0.20 × 0.20 mm
Pale yellow

Data collection

CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical ψ scans (North, Phillips & Mathews, 1968)
$T_{\min} = 0.955$, $T_{\max} = 0.998$
3531 measured reflections
3367 independent reflections

2085 reflections with $I > 2.5\sigma(I)$
$R_{\rm int} = 0.0084$
$\theta_{\max} = 25°$
$h = -12 \rightarrow 11$
$k = 0 \rightarrow 18$
$l = 0 \rightarrow 15$
3 standard reflections
frequency: 120 min
intensity decay: 3%

Refinement

Refinement on F
$R = 0.043$
$wR = 0.033$
$S = 2.80$
2085 reflections
245 parameters
H atoms calcutated, except those in N—H which were found from a ΔF map, and not refined
$w = 1/\sigma^2(F)$

$(\Delta/\sigma)_{\max} = 0$
$\Delta\rho_{\max} = 0.180$ e Å^{-3}
$\Delta\rho_{\min} = -0.250$ e Å^{-3}
Extinction correction: secondary
Extinction coefficient: 0.137631
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

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

O—C12	1.239 (3)	C1—C12	1.506 (3)
O—HN	2.435 (2)	C1—C13	1.499 (4)
N—C13	1.243 (3)	C2—C3	1.514 (3)
C1—C2	1.329 (3)	C2—C7	1.516 (3)
C2—C1—C12	121.7 (2)	O—C12—C1	119.5 (2)
C2—C1—C13	124.6 (2)	N—C13—C1	121.7 (2)
C12—C1—C13	112.8 (2)		
C2—C1—C12—O	89.2 (2)	C2—C1—C13—N	−124.5 (3)

Compound (3)

Crystal data

$C_{25}H_{24}O_2$
$M_r = 356.46$
Monoclinic
$C2/c$
$a = 15.460$ (7) Å
$b = 10.128$ (2) Å
$c = 12.680$ (3) Å
$\beta = 101.67$ (2)°
$V = 1944$ (1) Å^3
$Z = 4$
$D_x = 1.218$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 21.9$–$29.7°$
$\mu = 0.07$ mm^{-1}
$T = 298$ K
Tetragonal
0.50 × 0.35 × 0.20 mm
Pale yellow

Data collection

CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical ψ scans (North, Phillips & Mathews, 1968)
$T_{\min} = 0.863$, $T_{\max} = 0.999$
1786 measured reflections
1701 independent reflections

1214 reflections with $I > 2.5\sigma(I)$
$R_{\rm int} = 0.0049$
$\theta_{\max} = 25°$
$h = -18 \rightarrow 17$
$k = 0 \rightarrow 12$
$l = 0 \rightarrow 15$
3 standard reflections
frequency: 120 min
intensity decay: 3%

Refinement

Refinement on F
$R = 0.048$
$wR = 0.042$
$S = 4.70$
1214 reflections
125 parameters
H atoms calcutated
$w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{\max} = 0$

$\Delta\rho_{\max} = 0.18$ e Å^{-3}
$\Delta\rho_{\min} = -0.190$ e Å^{-3}
Extinction correction: secondary
Extinction coefficient: 0.661401
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 3. *Selected geometric parameters (Å, °) for (3)*

O—C8	1.224 (3)	C1—C8$^{\rm i}$	1.509 (3)
C1—C2	1.338 (5)	C2—C3	1.512 (3)
C1—C8	1.509 (3)	C2—C3$^{\rm i}$	1.512 (3)
C2—C1—C8	121.1 (2)	C1—C2—C3	124.1 (2)
C2—C1—C8—O	57.1 (2)		

Symmetry codes: (i) $-x, y, \frac{1}{2} - z$.

For all compounds, data collection: *NONIUS* (Riche, 1989); cell refinement: *NONIUS*; data reduction: *NRCVAX* (Larson *et al.*, 1990); program(s) used to solve structures: *NRCVAX*; program(s) used to refine structures: *NRCVAX*; molecular graphics: *ORTEP* (Johnson, 1965); software used to prepare material for publication: *NRCVAX*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: DE1050). Services for accessing these data are described at the back of the journal.

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(*tert*-Butoxycarbonylamino)acetonitrile†

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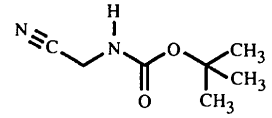
Abstract

The title compound, $C_7H_{12}N_2O_2$, is a useful intermediate for the synthesis of peptidic nucleic acids containing a backbone composed of repeating (2-aminoethyl)glycine units. Conjugation within the urethane system is facilitated by near planarity about both C—O and C—N bonds. There is a synperiplanar relationship between the O11 atom of the carbonyl group and the tertiary C7 atom, along with an antiperiplanar relationship between the C5 atom and the C10 methyl group.

Comment

Peptidic nucleic acids (PNAs) are useful nucleic acid mimetics which contain aminoethylglycine units in place of the conventional DNA sugar–phosphate backbone (Hyrup & Nielsen, 1996). PNAs containing the usual DNA bases (Egholm *et al.*, 1993) along with pseudoisocytosine (Egholm *et al.*, 1995) possess antisense/antigene properties (Noble *et al.*, 1995; Knudsen & Nielsen, 1996). Our interest in modulating the hydrogen-bonding interactions between PNA and DNA oligomers prompted an investigation of PNAs containing other purine bases such as xanthine and diaminopurine. The title compound, (1), is a key intermediate for the synthesis of the PNA backbone structure (Meltzer, Liang & Matsudaira, 1995; Ravikumar, 1994) which is available as an oil through acylation of aminoacetonitrile hydrochloride using di-Boc anhydride or on dehydration of 3-(*tert*-Boc-amino)ethanamide (Houssin, Bernier & Heinichart, 1988) (where Boc is butoxycarbonyl). We have successfully prepared (1) in crystalline form for the first time and here we compare its crystal structure with that of other Boc-protected analogues.



(1)

In common with other urethanes, the O6—C5—N4 bond angle is approximately 10° lower than the trigonal value. The *trans* orientation of the O11 atom compared to the H atom attached to N4 is a general feature among Boc-protected amino acids. Like Boc-protected glycine (Semertzidis *et al.*, 1989) and alanine (Benedetti *et al.*, 1981) structures, (1) has a synperiplanar relationship about the C5—O6 bond between the carbonyl O11 atom and the tertiary C7 atom, as well as an antiperiplanar disposition of one methyl group (C10) to the carbonyl C5 atom. However, the locations of the multiply bonded C atom, C2, in (1) and the carboxyl C atom in the amino acids, show more variability: C2—C3—N4—C5 is (−)-synclinal in (1) but ranges from 62.9 to 110.7° in the latter. N4, the only proton donor group, donates a fairly weak intermolecular hydrogen bond to a nearby N1 atom related by ($2 - x$, $-0.5 + y$, $0.5 - z$) with H4···N1 2.37 (2) Å and N4···N1 3.132 (2) Å.

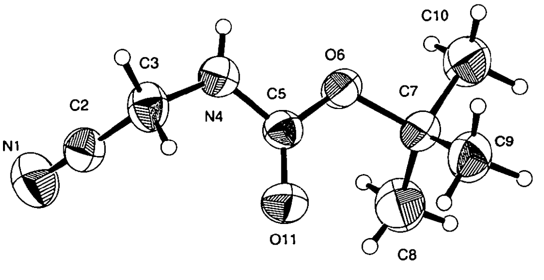


Fig. 1. *ORTEP*II view (Johnson, 1976) of the molecule. Displacement ellipsoids are drawn at the 50% probability level. H atoms are drawn as small spheres of arbitrary radius.

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† Alternative name: *tert*-butyl 3-cyano-2-azapropanoate.