of the occupation factor for O1W led to $x = 0.334\,(5)$. The values quoted for the density *etc.* are for $x = 1/3$.

Programs used included *MolEN* (Fair, 1990) and *ORTEP* (Johnson, 1965).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and torsion angles have been deposited with the IUCr (Reference: CR1117). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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2,2-Dimethyl-5-(dimethylamino)indan-1,3-dione

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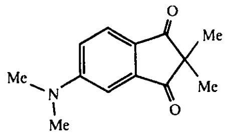
Abstract

The title compound, $C_{13}H_{15}NO_2$, lies on a crystallographic mirror plane. The indan-1,3-dione and the dimethylamino systems are therefore coplanar. The C—C—C angle formed by the *gem*-dimethyl groups is 110.3 (1)° and the C—C—C—O torsion angles which they form with the carbonyl O atoms have magnitudes of 61.6 (1) and 61.3 (1)°. The C=O distances are 1.217 (2) and 1.210 (2) Å. The *N*-methyl groups lying on the crystallographic mirror plane have their atoms disordered into half-populated positions. The N—C(methyl) distances are 1.432 (2) and 1.447 (2) Å.

Comment

As part of an ongoing study on nucleophilic aromatic substitution reactions with the fluoride ion, a number of substituted indan-1,3-diones were required (Enas, Garcia, Mathis & Gerdes, 1993). The crystal structures of a number of substituted indan-1,3-diones have been studied over the last 20 years on account of the well known anticoagulant activity of the parent compound in vitamin K-dependent biosynthesis (Ernster, Lind & Rase, 1972; Bravic, Gaultier & Hauw, 1974; Csöregh & Eckstein, 1979). The title compound, (I), was prepared in four steps from the known 2,2-dimethyl-1-indanone (Ohkata, Akiyama, Wada, Shun, Toda & Hanafusa, 1984), affording yellow needles when recrystallized by slow cooling and evaporation of ethanol.



(I)

The geometry about the N atom is perfectly planar, with angle magnitudes for C11—N—C5, C5—N—C12 and C11—N—C12 of 121.5 (1), 121.4 (1) and 117.1 (1)°, respectively. The *gem*-dimethyl groups are almost perfectly *gauche* to the carbonyl O atoms with magnitudes for C10—C9—C1—O1 and C10—C9—C8—O2 of 61.6 (1) and −61.3 (1)°, respectively, deviating only slightly from the perfect *gauche* conformation value of 60° (Klyne & Prelog, 1960).

Structural data for 2-ethyl-2-nitroindan-1,3-dione (Garcia, Enas, Chang & Fronczek, 1993), 5-amino-2,2-dimethylindan-1,3-dione and 2,2-dimethyl-5-nitroindan-1,3-dione (Garcia, Enas & Fronczek, 1993), 2-nitroindan-1,3-dione dihydrate (Selenius & Lundgren, 1980), and 2-(2-nitrobenzylidene)indan-1,3-dione (Varghese, Srinivasan, Ramadas & Padmanabhan, 1986) are in agreement with those of the title compound. Examples of planar dimethylamino-aromatic groups in agreement with that of the title compound are *trans*-1-(2-chloro-4-dimethylaminophenyl)-2-nitroethylene (Cameron, Cowley & Thompson, 1974), *N*,*N*-dimethyl-2,4-dinitro-3-toluidine (Maurin & Krygowski, 1987) and 9-(4-dimethylamino-2-methylphenyl)-10-methylacridinium chloride dihydrate (Reiss, Goubitz & Heijdenrijk, 1989).

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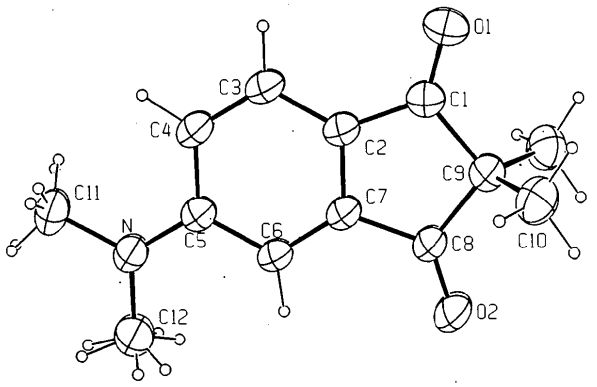

Fig. 1. *ORTEP* drawing (Johnson, 1965) of the molecule, representing heavy atoms as 40% probability ellipsoids and H atoms as circles of arbitrary radii. For *N*-methyl groups, both sets of half-populated H atoms are illustrated.

Experimental

Crystal data

$C_{13}H_{15}NO_2$
$M_r = 217.3$
Monoclinic
$P2_1/m$
$a = 8.7031\ (8)$ Å
$b = 7.3745\ (3)$ Å
$c = 9.1677\ (4)$ Å
$\beta = 97.694\ (5)°$
$V = 583.1\ (1)$ Å^3
$Z = 2$
$D_x = 1.237$ Mg m^{-3}

Cu $K\alpha$ radiation
$\lambda = 1.54184$ Å
Cell parameters from 25 reflections
$\theta = 20–39°$
$\mu = 0.64$ mm^{-1}
$T = 295$ K
Needle fragment
$0.60 \times 0.48 \times 0.17$ mm
Yellow
Crystal source: recrystallized from ethanol

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: empirical
$T_{\min} = 0.825$, $T_{\max} = 0.999$
2520 measured reflections
1302 independent reflections
1167 observed reflections
$[I > 3\sigma(I)]$

$R_{\rm int} = 0.023$
$\theta_{\max} = 75°$
$h = 0 \rightarrow 10$
$k = -8 \rightarrow 9$
$l = -11 \rightarrow 11$
3 standard reflections
frequency: 167 min
intensity variation: −2.6% (linear correction)

Refinement

Refinement on F
$R = 0.044$
$wR = 0.068$
$S = 3.558$
1167 reflections
116 parameters
$w = 4F_o^2/[\sigma^2(I) + (0.02F_o^2)^2]$
$(\Delta/\sigma)_{\max} = 0.01$
$\Delta\rho_{\max} = 0.28$ e Å^{-3}
$\Delta\rho_{\min} = -0.22$ e Å^{-3}

Extinction correction: $1/(1 + gI_c)$ applied to F_c
Extinction coefficient: $2.39\ (7) \times 10^{-5}$
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Tables 2.2B, 2.3.1)

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

$$B_{\rm eq} = (8\pi^2/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$B_{\rm eq}$
O1	0.1879 (2)	1/4	0.0696 (1)	5.73 (3)
O2	−0.0489 (1)	1/4	0.5032 (1)	6.00 (4)
N	0.5533 (1)	1/4	0.7404 (1)	4.44 (3)
C1	0.1661 (2)	1/4	0.1980 (2)	3.90 (3)
C2	0.2845 (2)	1/4	0.3272 (1)	3.47 (3)
C3	0.4464 (2)	1/4	0.3378 (2)	4.06 (3)
C4	0.5338 (2)	1/4	0.4742 (2)	3.93 (3)
C5	0.4645 (2)	1/4	0.6061 (1)	3.42 (3)
C6	0.3010 (1)	1/4	0.5938 (1)	3.51 (3)
C7	0.2162 (1)	1/4	0.4562 (2)	3.36 (2)
C8	0.0454 (2)	1/4	0.4176 (2)	3.82 (3)
C9	0.0062 (2)	1/4	0.2504 (2)	3.79 (3)
C10	−0.0852 (1)	0.0804 (2)	0.1982 (1)	4.98 (3)
C11	0.7208 (2)	1/4	0.7542 (2)	5.24 (4)
C12	0.4846 (2)	1/4	0.8738 (2)	6.38 (6)

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

O1—C1	1.217 (2)	C2—C7	1.393 (2)
O2—C8	1.210 (2)	C3—C4	1.374 (2)
N—C5	1.363 (2)	C4—C5	1.422 (2)
N—C11	1.447 (2)	C5—C6	1.412 (2)
N—C12	1.432 (2)	C6—C7	1.373 (2)
C1—C2	1.462 (2)	C7—C8	1.482 (2)
C1—C9	1.532 (2)	C8—C9	1.525 (2)
C2—C3	1.399 (2)	C9—C10	1.525 (2)
C5—N—C11	121.5 (1)	C5—C6—C7	119.0 (1)
C5—N—C12	121.4 (1)	C2—C7—C6	122.8 (1)
C11—N—C12	117.1 (1)	C2—C7—C8	109.0 (1)
O1—C1—C2	126.8 (1)	C6—C7—C8	128.2 (1)
O1—C1—C9	124.7 (1)	O2—C8—C7	126.3 (1)
C2—C1—C9	108.6 (1)	O2—C8—C9	124.9 (1)
C1—C2—C3	130.6 (1)	C7—C8—C9	108.8 (1)
C1—C2—C7	110.7 (1)	C1—C9—C8	103.0 (1)
C3—C2—C7	118.8 (1)	C1—C9—C10	111.07 (8)
C2—C3—C4	119.5 (1)	C3—C4—C5	121.9 (1)
C8—C9—C10	110.64 (8)	N—C5—C4	120.9 (1)
N—C5—C6	121.0 (1)	C10—C9—C10′	110.3 (1)
C4—C5—C6	118.0 (1)		
O1—C1—C9—C10	61.6 (1)	O2—C8—C9—C10	−61.3 (1)
C2—C1—C9—C10	−118.4 (1)	C7—C8—C9—C10	118.7 (1)

The space group was determined by systematic absences 0*k*0 with *k* odd and successful refinement of a centrosymmetric model. H atoms were refined isotropically, except for those on C11 and C12, which are disordered. Those were modelled with two sets of half-populated positions, with C—H = 0.95 Å and $B_{\rm iso} = 1.3B_{\rm eq}$ of the bonded C atom. Programs used were *MolEN* (Fair, 1990), *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980) and *ORTEP* (Johnson, 1965).

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Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: HU1092). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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1-Diphenylphosphino-2-methyl-1,2-dicarba-*closo*-dodecaborane(12)

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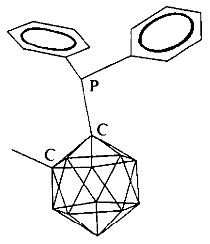
Abstract

Two C atoms from two phenyl groups and one C atom of the 2-methyl-1,2-dicarba-*closo*-dodecaborane cage in the title compound, $C_{15}H_{23}B_{10}P$, are bonded to the P atom in a pyramidal arrangement. In the carbaborane moiety, the C—C bond length is 1.702 (6) Å; lengthening of this bond is discussed.

Comment

1-Diphenylphosphino-2-methyl-1,2-dicarba-*closo*-dodecaborane (I) is an exceptionally stable compound which has the potential for extensive derivatization, both of the carbaborane polyhedron and of the phosphine moiety. The latter may be of interest in the search for new compounds of phosphines.



(I)

Surprisingly, there is no report in the literature on the use of this phosphine nor of similar compounds containing the *nido* derivative $[7\text{-}(PPh_2)\text{-}8\text{-}Me\text{-}nido\text{-}C_2B_9H_{10}]^-$. We have studied several thioxaether macrocycles of different ring sizes (9, 12 and 13 atoms) containing as a ring component the *closo*-borane moiety with sulfur, silicon or carbon directly bonded to the cluster C atoms. As a general trend, in the compounds substituted with sulfur the cluster C(1)—C(2) distance is longer than in the unsubstituted compounds or in compounds substituted with silicon or carbon. In the compounds containing two S atoms (Table 1), the C(1)—C(2) distance is 1.858 (5) and 1.826 (5) Å (Teixidor, Viñas, Rius, Miravitlles & Casabó, 1990) and 1.816 (6) Å (Teixidor, Romerosa, Rius, Miravitlles, Casabó, Viñas & Sanchez, 1990), whereas in 9,12-isopropylidenedithio-1,2-dicarba-*closo*-dodecaborane(12), a compound with unsubstituted cluster C atoms, it is only 1.634 (3) Å (Šubrtová, Línek & Hašek, 1980). Similarly, when the cluster C atoms are connected directly to silicon the C(1)—C(2) distance is 1.688 (5) Å (Kivekäs, Romerosa & Viñas, 1994), and when connected to carbon, 1.684 (6) Å (Holbrey, Iveson, Lockhart, Tomkinson, Teixidor, Romerosa, Viñas & Rius, 1993).

Apart from the crowding effects noted by Lewis & Welch (1993), another reason for C(cage)—C(cage) bond lengthening could be the partial overlap of the tangentially oriented *p* atomic orbitals (AO's) of the cluster CH unit with appropriate-symmetry AO's of the exocluster atom connected to the cluster C atom. Such an explanation is indicated schematically for