

Coordination of B and of C(1) is essentially planar [r.m.s. $\Delta = 0.008$ (4) Å for C₂BN, 0.004 (4) Å for NCC₂]. These two planes are mutually approximately perpendicular [dihedral angle = 94.4 (4)°]. The molecule thus has an allene-like structure. The short B–N and N–C bonds and virtually linear B–N–C indicate considerable π -bonding in these two bonds, in accordance with this description. Large deviations from linearity for M–N–C linkages in methyleneaminometalloid compounds have been taken to indicate little or no π -bonding when M = Ge or Sn (Alcock *et al.*, 1975), but steric factors can produce deviations of up to 20° from linearity even when π -bonding is considered to be very substantial (Shearer *et al.*, 1971; Hall *et al.*, 1979). In Ph₂BNCBu₂ the deviation is negligible.

Steric effects prevent both Ph groups from being coplanar with the C₂BN unit. Angles subtended by the two rings with this unit are 8.0 (4)° [C(11)–C(16); r.m.s. $\Delta = 0.004$ (3) Å] and 43.6° [C(21)–C(26); r.m.s. $\Delta = 0.007$ (3) Å]. No shortening of the B–C(11) bond relative to B–C(21) as a result of conjugation is, however, observed. The opening up of the C(11)–B–C(21) and C(2)–C(1)–C(6) angles above 120° may also be ascribed to steric interaction of the two Ph and of the two Bu substituents.

The NCBu₂ ligand geometry in Ph₂BNCBu₂ is virtually identical to that reported (Jennings, Snaith, Mahmoud, Wallwork, Bryan, Halfpenny, Petch & Wade, 1983) for the tris(methyleneamino)borane B(NCBu₂)₃, which has a paddle-wheel-shaped struc-

ture, with three allene-like B=N=C units with B–N and N–C distances of 1.39 and 1.23 Å respectively, BNC angles of 166°, mutually perpendicular BN₃ and BNC₂ planes, and $\nu(\text{C}=\text{N})$ (KBr disc) 1735 cm⁻¹.

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4,4,8 α -Trimethyl-8 $\alpha\beta$ -methoxycarbonyl-4 $\alpha\beta$,5,8,8 α -tetrahydro-1(4*H*)-naphthalenone,* C₁₅H₂₀O₃

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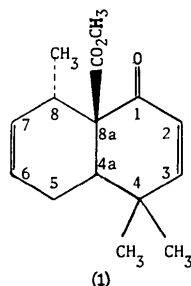
Abstract. $M_r = 248.32$, triclinic, $P\bar{1}$, $a = 8.308$ (3), $b = 11.649$ (4), $c = 8.233$ (3) Å, $\alpha = 98.16$ (3), $\beta = 111.63$ (3), $\gamma = 106.14$ (3)°, $V = 684.4$ (5) Å³, $Z = 2$, $D_x = 1.205$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 0.77$ cm⁻¹, $F(000) = 268$, $T = 295$ K, final $R = 0.065$ for 1011 observed reflections. The half-chair cyclohexene ring is *cis*-fused to a half-chair cyclohexenone ring. Although the packing arrangement is ideally suited

for [2 + 2] photodimerization, the molecule is photochemically inert in the solid state due to steric compression between the potentially reacting molecules and their stationary lattice neighbours.

Introduction. Irradiation of (1) in solution yields the cage compound resulting from intramolecular [2 + 2] cycloaddition. However, compound (1) is photochemically inert when irradiated in the solid state (Ariel, Askari, Scheffer, Trotter & Walsh, 1984). The present crystallographic study was undertaken to

* IUPAC name: methyl 1,1,5 α -trimethyl-4-oxo-1,4,4a,5,8,8 $\alpha\beta$ -hexahydronaphthalene-4 $\alpha\beta$ -carboxylate.

establish whether the crystal structure and the molecular conformation can explain the photo-inertness in the solid state.



Experimental. Crystal $0.1 \times 0.2 \times 0.3$ mm, m.p. 331–332 K, CAD-4 diffractometer, graphite-monochromatized $\text{Mo K}\alpha$ radiation, lattice parameters from setting of 25 reflections with $13 \leq \theta \leq 20^\circ$. 1832 unique reflections with $\theta \leq 25^\circ$, range of hkl : $-9 \rightarrow 9$, $-13 \rightarrow 13$, $0 \rightarrow 9$, ω - θ scan, ω scan width $(1.0 + 0.3 \tan \theta)^\circ$, extended 25% on each side for background measurement, horizontal aperture $(1.0 + \tan \theta)$ mm, vertical aperture 4 mm. Lp corrections. Three standard reflections, 13% decay. Structure solved by direct methods using *SHELX76* (Sheldrick, 1976) and refined by full-matrix least squares minimizing $\sum w(|F_o| - |F_c|)^2$. Four H atoms, H(2), H(3), H(6) and H(7), located in a difference synthesis; positions of all other H atoms calculated, methyl H atoms refined as rigid CH_3 groups possessing C_3 symmetry. Temperature factors of all H atoms refined isotropically. 207 parameters consisting of 78 positional parameters, 108 anisotropic temperature factors, 20 isotropic temperature factors and a scale factor. Final $R = 0.065$, $R_w = 0.047$ for 1011 reflections for which $F \geq 3\sigma(F)$, where $\sigma^2(I) = S + 2B + [0.04(S - B)]^2$, $S = \text{scan count}$, $B = \text{time-averaged background count}$. $R = 0.143$, $R_w = 0.067$ for all data, $w = 1/\sigma^2(F)$. $(\Delta/\sigma)_{\text{max}} = 0.2 \pm 0.24 \text{ e } \text{\AA}^{-3}$ in final difference synthesis. Atomic scattering factors from Cromer & Mann (1968) and Stewart, Davidson & Simpson (1965).

Discussion. Final atomic coordinates are in Table 1, bond distances and bond angles in Table 2.* The half-chair cyclohexene ring is *cis*-fused to a half-chair cyclohexenone ring (Fig. 1). The degree of twist in the conformation is described by the C(1)–C(8a)–C(4a)–C(5) torsion angle of $64.3(5)^\circ$. The spatial consequence of this arrangement is the proximity of the

β -enone carbon, C(3), to H(51) (2.77 Å). Furthermore, the angle between the C(3)–H(51) vector and its projection on the plane of the C(3)=C(2) double bond [C(1),C(2),C(3),C(4)], τ_c , is 58° . This geometry is

Table 1. Final coordinates ($\times 10^4$) and equivalent isotropic temperature factors ($\text{\AA}^2 \times 10^3$)

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

	x	y	z	U_{eq}
O(1)	6708 (5)	2840 (3)	7359 (6)	90
O(2)	4233 (4)	4579 (3)	7821 (4)	59
O(3)	1673 (4)	3223 (3)	7746 (4)	58
C(1)	5218 (8)	2847 (4)	6328 (9)	59
C(2)	5011 (10)	3344 (5)	4751 (10)	73
C(3)	3385 (10)	3161 (5)	3444 (10)	73
C(4)	1542 (7)	2395 (4)	3329 (7)	62
C(41)	504 (8)	3254 (5)	3625 (8)	83
C(42)	348 (10)	1544 (6)	1357 (8)	97
C(4a)	1851 (6)	1614 (4)	4720 (6)	50
C(5)	2218 (7)	459 (4)	4006 (7)	61
C(6)	3021 (8)	-145 (5)	5435 (11)	69
C(7)	3612 (8)	341 (5)	7168 (11)	73
C(8)	3544 (6)	1561 (4)	7953 (7)	57
C(81)	5072 (8)	2193 (5)	9901 (7)	81
C(8a)	3454 (6)	2380 (4)	6620 (6)	43
C(8a1)	3185 (7)	3521 (5)	7451 (6)	46
C(9)	1311 (8)	4264 (5)	8544 (9)	74

Table 2. Bond lengths (Å) and bond angles ($^\circ$)

C(1)–O(1)	1.218 (8)	C(5)–C(6)	1.497 (11)
C(1)–C(2)	1.468 (11)	C(6)–C(7)	1.303 (11)
C(1)–C(8a)	1.535 (10)	C(7)–C(8)	1.501 (10)
C(2)–C(3)	1.316 (12)	C(8)–C(8a)	1.548 (9)
C(3)–C(4)	1.503 (11)	C(8a)–C(8a1)	1.519 (9)
C(4)–C(4a)	1.554 (9)	C(8)–C(81)	1.540 (10)
C(4)–C(41)	1.540 (10)	C(8a1)–O(2)	1.212 (7)
C(4)–C(42)	1.553 (9)	C(8a1)–O(3)	1.328 (7)
C(4a)–C(5)	1.545 (8)	C(9)–O(3)	1.455 (7)
C(4a)–C(8a)	1.557 (8)		
C(2)–C(1)–O(1)	121.9 (8)	C(7)–C(6)–C(5)	123.7 (9)
C(3)–C(2)–C(1)	122.9 (9)	C(8)–C(7)–C(6)	123.8 (9)
C(8a)–C(1)–O(1)	122.5 (9)	C(8a)–C(8)–C(7)	110.8 (7)
C(8a)–C(1)–C(2)	115.5 (8)	C(81)–C(8)–C(7)	111.9 (7)
C(4)–C(3)–C(2)	125.2 (10)	C(8a)–C(8)–C(81)	115.3 (6)
C(4a)–C(4)–C(3)	109.4 (8)	C(8)–C(8a)–C(1)	114.9 (6)
C(41)–C(4)–C(3)	109.4 (7)	C(4a)–C(8a)–C(1)	106.5 (6)
C(42)–C(4)–C(3)	108.0 (8)	C(8)–C(8a)–C(4a)	109.2 (5)
C(4a)–C(4)–C(41)	112.9 (7)	C(8a1)–C(8a)–C(1)	106.8 (6)
C(4a)–C(4)–C(42)	111.1 (6)	C(8a1)–C(8a)–C(4a)	113.2 (5)
C(42)–C(4)–C(41)	105.9 (7)	C(8a1)–C(8a)–C(8)	106.4 (6)
C(5)–C(4a)–C(4)	111.3 (6)	C(8a)–C(8a1)–O(2)	124.2 (7)
C(8a)–C(4a)–C(4)	112.9 (5)	C(8a)–C(8a1)–O(3)	111.9 (6)
C(8a)–C(4a)–C(5)	109.5 (6)	O(3)–C(8a1)–O(2)	123.9 (6)
C(6)–C(5)–C(4a)	114.1 (7)	C(9)–O(3)–C(8a1)	115.5 (5)

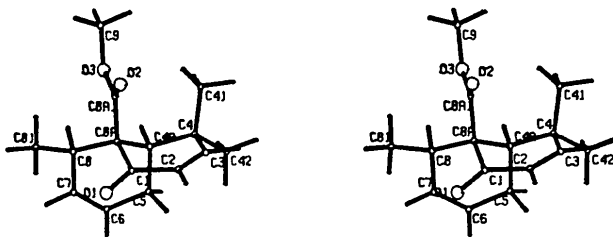


Fig. 1. Stereoscopic view of (1) with atomic labelling.

* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and bond distances and angles involving H atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39666 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

highly favourable for H abstraction by the β -enone C (Jiang, Scheffer, Secco & Trotter, 1981), yet compound (1) is photo-inert in the solid state. The reason for the lack of reactivity is shown in Fig. 1. Abstraction of H(51) by C(3) is sterically hindered by the methyl group C(42) [H(421)⋯H(51) is 2.2 Å]. Abstraction of H(51) by the α -enone C [C(2)⋯H(51) is 2.84 Å] is not sterically hindered by the methyl H atoms on C(42); however, abstraction by C(2) would lead to an unstable radical on C(3), in an α -position relative to dimethylated C(4).

It is noteworthy that O abstraction of a β -H from C(8) cannot occur because of unsuitable geometry. Molecule (1) adopts a common conformation in which the bulkier substituent on C(8) assumes the pseudo-equatorial position, with H(8) in the pseudo-axial position, 3.92 Å from O(1).

Bond lengths and angles (Table 2) do not deviate significantly from accepted values. C(4)–C(4a) and C(4a)–C(8a) bonds are relatively long [1.554 (9) and 1.557 (8) Å respectively] because of steric effects due to the methyl groups on C(4) and the ester on C(8a).

A stereodiagram of compound (1) and its nearest lattice neighbours is shown in Fig. 2. The centrosymmetrically related molecules X and \bar{X} are ideally arranged to undergo [2 + 2] photodimerization. The potentially reactive enone double bonds are parallel, directly above one another and only slightly offset along the double-bond axis (0.52 Å); the centre-to-centre distance is 3.79 (1) Å. Crystal structures and photochemical studies of a series of *cis*-4a,5,8,8a-tetrahydro-1,4-naphthoquinone derivatives have revealed that the most favourable reaction involves [2 + 2] intermolecular cycloaddition in the solid state for those crystals with parallel C=C bonds in adjacent molecules with a separation of <4.1 Å (Trotter, 1983). Nevertheless, compound (1) is photochemically inert when irradiated in the solid state (Ariel *et al.*, 1984). Inspection of the packing diagram (Fig. 2) reveals the probable answer to the source of this remarkable lack of reactivity in the solid state. As the potentially reactive molecules X and \bar{X} start to move towards one

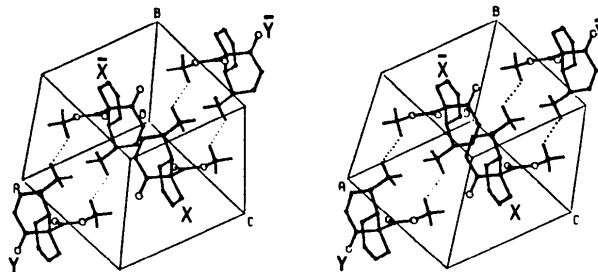


Fig. 2. Stereopacking diagram of (1). Molecules X and \bar{X} are related through a centre of symmetry. Translation of X along a generates Y , and translation of \bar{X} along $-a$ generates \bar{Y} . The dotted lines indicate the intermolecular H⋯H repulsion. For clarity of the picture certain atoms are omitted: methyl groups C(42) and C(81), and all H atoms, except those on C(41) and C(9).

another in the initial stages of [2 + 2] photocycloaddition, each experiences increasingly severe steric compression of two of its methyl groups (dotted lines). The key feature of this steric compression is that it is developed, not between the potential reactants X and \bar{X} , but between X and \bar{Y} and \bar{X} and Y . Thus molecules Y and \bar{Y} act as stationary impediments to the dimerization.

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Structure of 4-*p*-Chlorophenyl-1-methyl-2,6-diphenylpyridinium Iodide, C₂₄H₁₉ClN⁺.I⁻

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Abstract. $M_r = 438.733$, monoclinic, $P2_1/n$, $a = 1.35(2) \text{ g cm}^{-3}$, $\text{Mo K}\alpha$, $\lambda = 0.7107 \text{ \AA}$, $\mu = 10.404(9)$, $b = 10.745(2)$, $c = 19.982(3) \text{ \AA}$, $\beta = 16.781 \text{ cm}^{-1}$, $F(000) = 860$, room temperature, final $R = 0.073$ for 2675 reflections. The molecule shows an

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