Acta Cryst. (1983). C**39**, 348–350

7-Isopropylidenebenzo-8,9,10-trinorbornadiene,* $C_{14}H_{14}$

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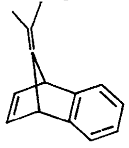
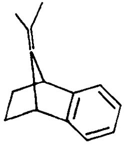
(*Received* 2 *August* 1982; *accepted* 13 *October* 1982)

Abstract. $M_r = 182\cdot27$, monoclinic, $P2_1/c$, $a = 13\cdot447\,(4)$, $b = 8\cdot081\,(1)$, $c = 11\cdot821\,(4)$ Å, $\beta = 125\cdot57\,(2)°$, $V = 1044\cdot8\,(5)$ Å^3, $Z = 4$, $D_x = 1\cdot16$ Mg m^{-3}, λ(Cu $K\alpha$) = 1·54178 Å, $\mu = 0\cdot496$ mm^{-1}, room temperature. Final $R = 0\cdot042$ based on 624 unique observed reflections. The phenyl ring and attached atoms form a planar system while the two C atoms of the endocyclic double bond are slightly pyramidalized. The planar isopropylidene moiety is bent toward the phenyl ring.

Introduction. 7-Isopropylidenebenzo-8,9,10-trinorbornadiene (1) is of synthetic and theoretical interest (Sasaki, Hayakawa, Manabe & Nishida, 1981). The small energy separation between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) enable it to participate in both HOMO-controlled and LUMO-controlled reactions (Houk, Sims, Watts & Luskus, 1973; Sustmann, 1971). In Diels–Alder reactions addition occurs at the endocyclic double bond with enhanced rates for the HOMO-controlled reactions but with normal rates for the LUMO-controlled reactions. Reactions involving polarized transition states occur at the exocyclic double bond. Singlet oxygen adds stereoselectively to 7-isopropylidenebenzo-8,9,10-trinorbornene (2) and its derivatives. It has been suggested that π-orbital distortion of the exocyclic double bond is the most important factor controlling this addition (Okada & Mukai, 1979; Paquette, Hertel, Gleiter & Bohm, 1978). Since the π-orbital distortion (pyramidalization), as revealed by X-ray diffraction studies (Watson, Galloy, Bartlett & Roof, 1981; Pinkerton, Schwarzenbach, Stibbard, Carrupt & Vogel, 1981), significantly affects the rates and stereochemistry of electrophilic additions to 8,9,10-trinorbornenes, the crystal structure of (1) should provide additional insight into these important compounds.


(1)


(2)

Experimental. Synthesized by reaction of 6,6-dimethylfulvene with benzyne (Muneyuki & Tanida, 1966), recovered solid recrystallized from ethanol; in presence of air crystals decompose when exposed to X-rays but are stable when enclosed in a capillary; parallelepiped, 0·2 × 0·3 × 0·3 mm, Syntex $P2_1$ diffractometer, θ:2θ scanning technique, $2\theta_{\max} = 120°$, graphite-monochromatized Cu $K\alpha$ radiation, lattice parameters refined by least-squares utilizing 15 medium-angle reflections (angles measured by a centering routine associated with the diffractometer), systematic absences ($l = 2n+1$ for $h0l$; $k = 2n+1$ for $0k0$) consistent with space group $P2_1/c$, $F(000) = 392$; a periodically monitored reflection showed no change in intensity greater than $2\sigma(I)$, 1462 independent reflections ($-13 \leq h \leq 12$, $k \leq 8$, $l \leq 12$), 624 observed with $I > 3\sigma(I)$, Lorentz and polarization corrections applied, no absorption corrections made; direct-methods program *MULTAN* 78 (Main, Lessinger, Woolfson, Germain & Declercq, 1978) revealed positions of all non-H atoms; after several cycles of least-squares refinement of C atoms with anisotropic thermal parameters H atoms located in a difference Fourier map; full-matrix least-squares refinement with isotropic thermal parameters for H atoms led to final values $wR = 0\cdot057$ and $S = 3\cdot67$, function minimized $\sum w(|F_o| - |F_c|)^2$ where $w = 1/\sigma^2(F_o)$, largest peak in final difference Fourier map 0·2e Å^3 and average and maximum shift/error 0·004 and 0·02 respectively; atomic scattering factors calculated by XRAY 76 program (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976), locally written programs used for data reduction and initial block-diagonal least-squares refinement, *MULTAN* 78 used for direct-methods calculations and XRAY 76 for all other computations.

Discussion. Table 1 gives a listing of atomic positional parameters while Table 2 lists interatomic distances and valence angles.†

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* Alternative nomenclature: 1,4-isobuteno-1,4-dihydronaphthalene.

† Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38180 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

0108-2701/83/030348-03$01.50

Table 1. *Atomic positional* ($\times 10^4$, H *atoms* $\times 10^3$) *and isotropic thermal parameters* (Å^2)

	x	y	z	U_{eq}*
C(1)	2633 (6)	4821 (8)	−764 (6)	40
C(2)	2389 (5)	3046 (8)	−540 (6)	38
C(3)	1814 (5)	3143 (8)	136 (6)	39
C(4)	1702 (6)	4988 (8)	343 (7)	41
C(5)	835 (6)	5709 (9)	−1130 (8)	53
C(6)	1365 (6)	5608 (8)	−1774 (8)	49
C(7)	2915 (6)	5559 (7)	605 (7)	38
C(8)	3850 (6)	6392 (7)	1610 (7)	41
C(9)	4936 (7)	6828 (10)	1610 (9)	56
C(10)	3916 (8)	6989 (11)	2855 (8)	60
C(11)	2636 (6)	1542 (9)	−877 (6)	44
C(12)	2298 (7)	116 (9)	−510 (8)	53
C(13)	1724 (7)	218 (9)	147 (8)	54
C(14)	1474 (6)	1737 (9)	492 (7)	49
H(1)	326 (5)	494 (7)	−98 (6)	51†
H(4)	155 (5)	533 (6)	115 (6)	51
H(5)	4 (5)	599 (7)	−144 (6)	51
H(6)	105 (5)	592 (7)	−276 (6)	51
H(9*a*)	572 (6)	647 (8)	243 (7)	63
H(9*b*)	488 (5)	625 (7)	78 (6)	63
H(9*c*)	505 (6)	794 (8)	159 (7)	63
H(10*a*)	402 (6)	807 (8)	305 (7)	63
H(10*b*)	319 (6)	679 (8)	280 (6)	63
H(10*c*)	454 (6)	647 (8)	369 (7)	63
H(11)	304 (5)	146 (7)	−141 (6)	51
H(12)	246 (5)	−92 (7)	−71 (6)	51
H(13)	151 (5)	−74 (7)	48 (6)	51
H(14)	109 (5)	182 (7)	103 (6)	51

* $U_{eq} = \frac{1}{3}\sum_i \sum_j U_{ij} a_i^* a_j^* (\mathbf{a}_i . \mathbf{a}_j) \times 10^3$.

† H-atom thermal parameters = $U_{iso} \times 10^3$.

Table 2. *Interatomic distances* (Å) *and valence angles* (°)

C(1)—C(2)	1·53 (1)	C(4)—C(7)	1·54 (1)
C(1)—C(6)	1·540 (9)	C(5)—C(6)	1·31 (2)
C(1)—C(7)	1·55 (1)	C(7)—C(8)	1·307 (8)
C(2)—C(3)	1·40 (1)	C(8)—C(9)	1·50 (1)
C(2)—C(11)	1·38 (1)	C(8)—C(10)	1·50 (1)
C(3)—C(4)	1·53 (1)	C(11)—C(12)	1·40 (1)
C(3)—C(14)	1·38 (1)	C(12)—C(13)	1·38 (2)
C(4)—C(5)	1·539 (9)	C(13)—C(14)	1·40 (1)

C(2)—C(1)—C(6)	105·6 (5)	C(4)—C(5)—C(6)	108·8 (7)
C(2)—C(1)—C(7)	97·3 (6)	C(1)—C(6)—C(5)	107·8 (7)
C(6)—C(1)—C(7)	98·0 (6)	C(1)—C(7)—C(4)	95·0 (5)
C(1)—C(2)—C(3)	107·0 (6)	C(1)—C(7)—C(8)	132·0 (9)
C(1)—C(2)—C(11)	131·7 (8)	C(4)—C(7)—C(8)	133·0 (9)
C(3)—C(2)—C(11)	121·3 (7)	C(7)—C(8)—C(9)	122·8 (9)
C(2)—C(3)—C(4)	106·5 (7)	C(7)—C(8)—C(10)	122·2 (9)
C(2)—C(3)—C(14)	121·3 (7)	C(9)—C(8)—C(10)	114·9 (6)
C(4)—C(3)—C(14)	132·2 (9)	C(2)—C(11)—C(12)	117·4 (9)
C(3)—C(4)—C(5)	105·5 (6)	C(11)—C(12)—C(13)	121·0 (8)
C(3)—C(4)—C(7)	97·6 (6)	C(12)—C(13)—C(14)	121·8 (8)
C(5)—C(4)—C(7)	97·5 (7)	C(3)—C(14)—C(13)	117·1 (9)

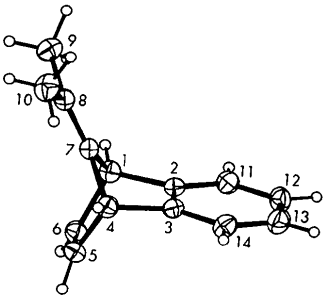

Fig. 1. *ORTEP* drawing of 7-isopropylidenebenzo-8,9,10-trinorbornadiene. The thermal ellipsoids are drawn at 35% probability level. H atoms are represented by spheres of arbitrary radius.

Fig. 1 is an *ORTEP* drawing (Johnson, 1971) of compound (1). Although not required by space-group considerations, the molecule has C_s symmetry with all bonds related by the mirror plane being statistically equivalent. The phenyl ring is planar with a maximum deviation from the plane of 0·004 (2) Å by C(13). Atoms C(1)C(4)C(7)C(8)C(9)C(10) form a plane with a maximum deviation of 0·008 (4) Å by C(4). The interplanar angles involving the above plane and the planar segments C(1)C(2)C(3)C(4) and C(1)C(4)C(5)C(6) are 121·9 (4) and 124·9 (4)° respectively. The isopropylidene moiety is tilted toward the phenyl ring and away from the endocyclic double bond. The interplanar angle between C(1)C(4)C(5)C(6) and C(5)C(6)H(5)H(6) is 5·6 (7)° with the two H atoms bent away from the isopropylidene moiety. As an isolated observation the deviation from planarity might not be considered to be significant; however, the distortion is of the magnitude and direction observed for a number of 8,9,10-trinorbornene derivatives (Watson *et al.*, 1981; Pinkerton *et al.*, 1981; Watson, 1983). The pyramidalization of the C(5) and C(6) atoms results in a greater π-electron density on the isopropylidene face which leads to accelerated rates and stereospecific electrophilic additions (Rondan, Paddon-Row, Caramella & Houk, 1981; Wipff & Morokuma, 1980). The added electron density forces the isopropylidene moiety toward the phenyl ring which is coplanar with atoms C(1) and C(4).

The observed pyramidalization has been attributed to a hyperconjugative interaction with the C(1)—C(2) and C(4)—C(3) σ bonds or to torsional interactions with C(4)—H(4) and C(1)—H(1) (Watson, 1983). These two effects are not easily separable since they lead to identical distortions.

We thank The Robert A. Welch Foundation for their financial support (P–074). This is FASTBIOS contribution No. 99.

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Acta Cryst. (1983). C**39**, 350–353

Structure of an Adrenergic Drug: L-Phenylephrine Hydrochloride, $C_9H_{14}NO_2^+.Cl^-$

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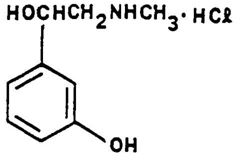
(*Received 5 April* 1982; *accepted* 27 *October* 1982)

Abstract. $M_r = 203{\cdot}7$, monoclinic, $P2_1$, $a = 14{\cdot}151$ (3), $b = 6{\cdot}790$ (2), $c = 11{\cdot}404$ (3) Å, $\beta = 103{\cdot}08$ (2)°, $V = 1067{\cdot}3$ Å^3, $Z = 4$, $D_x = 1{\cdot}267$ Mg m^{-3}, λ(Cu $K\alpha$) = 1·54184 Å, $\mu = 2{\cdot}93$ mm^{-1}, $T = 277 \pm 1$ K. Final R = 0·045 for 1434 observed reflections. Both the molecules in the asymmetric unit have extended *trans* conformations and the atoms in the two molecules are related by an approximate pseudo glide plane except for the ethanol OH group. The crystal structure is stabilized by a three-dimensional network of hydrogen bonds of types N–H···Cl, O–H···Cl and O–H···O.

Introduction. Phenylephrine (more commonly known as neosynephrine) hydrochloride, 1-(3-hydroxyphenyl)-2-methylaminoethanol hydrochloride, is a sympathomimetic drug and is used mainly as a nasal decongestant. Phenylephrine differs chemically from epinephrine only by lacking an –OH in the *para* position of the benzene ring. It was first studied by Barger & Dale (1910) but was not used clinically until years later when it was found to have greater potency, because of its direct action in receptors. Phenylephrine is a powerful postsynaptic α-receptor stimulant with little effect on the β-receptors of the heart (Weiner, 1980). The structure of L-phenylephrine (free-base form) was reported earlier (Andersen, 1976). It was thought worthwhile to look at the structure of the therapeutically prescribed form, L-phenylephrine hydrochloride, so that one can compare the structural and conformational features with those of the free base L-phenylephrine, synephrine (Dattagupta, Meyer & Mukhopadhyay, 1982), norsynephrine (Paxton & Hamor, 1977), and of other sympathomimetic drugs most of which are found to assume a preferred conformation in the crystalline state (Carlström, Bergin & Falkenberg, 1973). A preliminary account of this structure was reported earlier (Bhaduri & Saha, 1975), and the complete solution of the structure and its refined parameters are presented here.



Experimental. Aqueous solution of title compound (Sigma Chemical Co.) evaporated at 298 K, hy-

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