Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: CR1152). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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endo-3,3-Diphenyltricyclo[3.2.1.$0^{2,4}$]oct-6-ene

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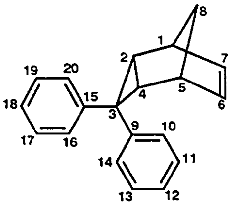
Abstract

The main feature in the title compound, $C_{20}H_{18}$, is the system of fused three-, five- and six-membered rings. The two phenyl substituents are bonded to one C atom of the three-membered ring and that ring adopts an *endo* conformation relative to the larger rings. This results in a phenyl-group atom being close to the diene bond in the fused rings. The contact distances are 2.912 (4) and 2.952 (3) Å. The plane of this phenyl group is nearly parallel to the diene bond. Planes of the two phenyl rings make an angle of 76.1 (2)°.

Comment

The compound is one of two test molecules being used in an ongoing study of reactions involving Long Range Aryl Migration with Electrocyclic Ring Opening (LRAMERO) (Wilt & Tufano, 1985). In particular, the *endo* compound has been used as a vehicle for probing aryl-π-participation in addition and solvolysis reactions (Peeran, Wilt, Subramanian & Crumrine, 1989, 1993). In order to elucidate the mechanism of these reactions it became important to establish intramolecular contact distances for *exo* and *endo* conformations. This paper reports the structure of the *endo* conformer.



The main feature in this structure is the system of fused three-, five- and six-membered rings. The three-membered ring contains two phenyl substituents at methylene C3. The *endo* conformation places C3 *anti* to C8 and at a contact distance of 3.419 (3) Å. Correspondingly, there are shorter contact distances from C3 to the double-bonded atoms C6 and C7 of 2.957 (3) and 2.980 (3) Å, respectively. The phenyl groups are bonded to C3 at C9 and C15, and short contact distances C9···C6 and C9···C7 of 2.912 (4) and 2.952 (3) Å are noted. The C9–C14 phenyl group is nearly planar to the double bond as evidenced by comparable contact distances of 3.251 (4) for C10···C7 and 3.146 (4) Å for C14···C6, and by a small angle of 3.0 (4)° between the C6–C7 vector and plane of the phenyl group. The angle between this vector and plane of the second phenyl group (C15–C20) is 7.0 (5)°. The planes of the two phenyl groups intersect at an angle of 76.1 (2)°. All bond lengths and angles within the phenyl groups are normal with average geometric parameters of 1.381 (11) Å and 120.0 (9)°.

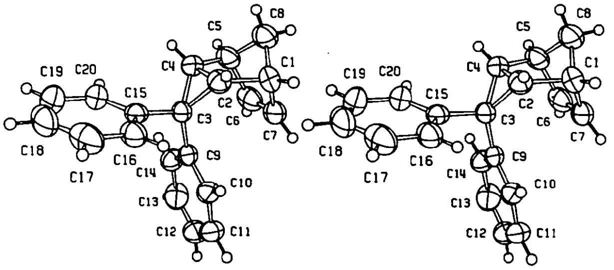


Fig. 1. An *ORTEP* (Johnson, 1976) stereoview of the molecule using displacement ellipsoids drawn at the 50% probability level. H atoms are shown as small spheres of arbitrary radius.

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† Deceased May 13 1987.

The structure of an *exo* conformer of unsubstituted tricyclo[3.2.1.$0^{2,4}$]oct-6-ene has been reported as a silver(I) π-complex (Gibbons & Trotter, 1971). In this case the contact distance C3···C8 is only 2.9 (1) Å, whereas contact distances C3···C6 and C3···C7 are both 3.8 (1) Å. Another difference between *exo* and *endo* structures lies in the 'hinge' angles involving bridgehead atoms C1 and C5 and atoms of the six-membered ring. In the *exo* case these angles are C2—C1—C7 97 (5) and C4—C5—C6 100 (5)°, and both are significantly smaller than found in the *endo* compound. This can be attributed to steric interaction between C3 and C8 in the *exo* conformer which operates to close the hinge, and between phenyl group C9–C14 and double bond C6═C7 in the *endo* conformer which operates to open the hinge.

Experimental

The compound was prepared by M. Peeran using three modifications to the procedure reported by Wilt & Sullivan (1975). (1) The first reaction step involving diphenyldiazomethane and 7-*tert*-butoxynorbornadiene was carried out at room temperature, (2) reaction products were separated from excess diene by distillation under reduced pressure and (3) the three-membered ring was formed by photolytic elimination of N_2 from the corresponding pyrazoline, using a 450 W medium-pressure UV source. Recrystallization from benzene afforded good quality crystals.

Crystal data

$C_{20}H_{18}$
$M_r = 258.36$
Triclinic
$P\overline{1}$
$a = 13.0681 (5)$ Å
$b = 6.1093 (2)$ Å
$c = 9.7006 (3)$ Å
$\alpha = 79.535 (2)°$
$\beta = 107.879 (2)°$
$\gamma = 93.968 (2)°$
$V = 724.7 (1)$ Å^3
$Z = 2$
$D_x = 1.18$ Mg m^{-3}

Cu $K\alpha$ radiation
$\lambda = 1.5418$ Å
Cell parameters from 21 reflections
$\theta = 30–37°$
$\mu = 0.47$ mm^{-1}
$T = 292$ K
Prism
0.30 × 0.26 × 0.21 mm
Colorless

Data collection

Modified Picker FACS–I diffractometer
$\theta/2\theta$ scans
Absorption correction: empirical from ψ scans with χ set at 90°
$T_{\min} = 0.87$, $T_{\max} = 0.91$
2553 measured reflections
2146 independent reflections
1743 observed reflections [$I > 3\sigma(I)$]

$R_{\rm int} = 0.047$
$\theta_{\max} = 60°$
$h = 0 \rightarrow 14$
$k = -6 \rightarrow 6$
$l = -10 \rightarrow 10$
4 standard reflections monitored every 150 reflections intensity decay: 6%

Refinement

Refinement on F
$R = 0.070$
$wR = 0.087$
$S = 0.8245$
1743 reflections
181 parameters
$w = 1/[\sigma^2(F) + 0.0187F^2]$
$(\Delta/\sigma)_{\max} = 0.006$

$\Delta\rho_{\max} = 0.25$ e Å^{-3}
$\Delta\rho_{\min} = -0.20$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2*B*)

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	$U_{\rm eq}$
C1	0.9238 (2)	0.4954 (4)	0.7436 (3)	0.056 (3)
C2	0.8793 (2)	0.4343 (4)	0.5867 (3)	0.047 (2)
C3	0.7971 (2)	0.2513 (4)	0.5424 (2)	0.040 (2)
C4	0.9148 (2)	0.1980 (4)	0.6074 (2)	0.048 (2)
C5	0.9757 (2)	0.1425 (4)	0.7758 (3)	0.054 (2)
C6	0.8995 (2)	0.1467 (5)	0.8637 (3)	0.060 (3)
C7	0.8691 (2)	0.3560 (5)	0.8463 (3)	0.065 (3)
C8	1.0316 (2)	0.3754 (5)	0.7943 (3)	0.065 (3)
C9	0.7087 (2)	0.1652 (4)	0.6093 (3)	0.041 (2)
C10	0.6326 (2)	0.3111 (5)	0.6129 (3)	0.049 (3)
C11	0.5489 (2)	0.2354 (6)	0.6673 (4)	0.062 (4)
C12	0.5369 (3)	0.0126 (7)	0.7153 (4)	0.072 (4)
C13	0.6113 (3)	−0.1345 (6)	0.7117 (4)	0.071 (4)
C14	0.6951 (2)	−0.0556 (5)	0.6548 (3)	0.055 (3)
C15	0.7552 (2)	0.2587 (4)	0.3770 (3)	0.045 (3)
C16	0.6984 (2)	0.4439 (5)	0.2867 (3)	0.054 (3)
C17	0.6564 (3)	0.4478 (7)	0.1376 (4)	0.072 (4)
C18	0.6713 (3)	0.2687 (9)	0.0758 (4)	0.087 (5)
C19	0.7293 (3)	0.0890 (7)	0.1643 (4)	0.084 (4)
C20	0.7705 (2)	0.0839 (5)	0.3134 (3)	0.060 (3)

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

C1—C2	1.558 (3)	C3—C9	1.510 (3)
C1—C7	1.508 (4)	C3—C15	1.521 (3)
C1—C8	1.533 (4)	C4—C5	1.566 (3)
C2—C3	1.521 (3)	C5—C6	1.502 (4)
C2—C4	1.506 (3)	C5—C8	1.568 (4)
C3—C4	1.506 (3)	C6—C7	1.331 (4)
C2—C1—C7	110.6 (2)	C3—C4—C5	125.2 (2)
C2—C1—C8	98.9 (2)	C4—C5—C6	110.2 (2)
C7—C1—C8	99.4 (2)	C4—C5—C8	97.8 (2)
C1—C2—C3	125.7 (2)	C6—C5—C8	98.7 (2)
C1—C2—C4	103.7 (2)	C5—C6—C7	108.2 (2)
C3—C2—C4	59.7 (2)	C1—C7—C6	107.1 (2)
C2—C3—C4	59.7 (2)	C1—C8—C5	92.7 (2)
C2—C3—C9	127.3 (2)	C3—C9—C10	119.9 (2)
C4—C3—C9	126.3 (2)	C3—C9—C14	121.7 (2)
C2—C3—C15	113.1 (2)	C10—C9—C14	118.2 (3)
C4—C3—C15	113.7 (2)	C3—C15—C16	119.8 (2)
C9—C3—C15	109.1 (2)	C3—C15—C20	121.4 (2)
C2—C4—C3	60.7 (2)	C16—C15—C20	118.8 (3)
C2—C4—C5	103.6 (2)		

Cell constant data were collected by ±2θ scans and parameters were determined from least-squares calculations which accounted for $K_{(\alpha1-\alpha2)}$ splitting. All H atoms were found in subsequent Fourier electron density difference maps. During refinement the H atoms were fixed in positions of idealized geometry with d(C—H) = 0.95 Å and U(H) = 0.06 Å^2.

Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELX*76 (Sheldrick, 1976). Molecular graphics: *ORTEP*II (Johnson, 1976).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AB1249). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Bromure de Benzododécinium Monohydraté

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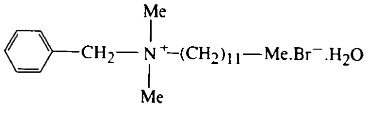
Abstract

The monohydrate of benzyldodecyldimethylammonium bromide, $C_{21}H_{38}N^{+}.Br^{-}.H_2O$, which has preservative properties, has been synthesized and its structure determined from single-crystal X-ray diffraction data. The aromatic ring plane and the C7—N8—C10 plane are orthogonal. Bond lengths and angles are in agreement with published values for similar compounds. The water molecule is linked to one of the methyl groups by a short van der Waals interaction.

Commentaire

Les ammoniums quaternaires sont souvent utilisés comme conservateurs dans l'industrie pharmaceutique. Cependant, lorsqu'ils se présentent sous forme solide, certains sont des mélanges, d'autres des composés plus ou moins hydratés, voire hygroscopiques (le chlorure de benzalkonium ou le cétrimide, par exemple). Ainsi le bromure de benzyldodécyldiméthylammonium ou bromure de benzododécinium (BBD) commercial, certes de composition chimique définie, est un solide hygroscopique, souvent aggloméré et pâteux, contenant environ 3% d'eau et pouvant s'hydrater. Afin d'obtenir un produit non hygroscopique, nous avons introduit lors de la synthèse de BBD une molécule d'eau afin d'accéder directement au monohydrate, qui par analogie avec le cétylpyridinium serait non hygroscopique. Effectivement, le nouveau procédé de synthèse (Stigliani *et al.*, 1993) permet d'obtenir de manière quantitative (rendement > 92%) une poudre blanche, non hygroscopique, stable avec une grande pureté (>99,5%). Le but de l'étude cristallographique est de préciser la géométrie de la molécule et de confirmer son degré d'hydration.



$$C_6H_5-CH_2-\overset{\text{Me}}{\underset{\text{Me}}{N^{+}}}-(CH_2)_{11}-\text{Me}.Br^{-}.H_2O$$

BBD.H_2O

Le cycle benzénique (Fig. 1) est plan. La valeur du paramètre χ^2 relative à son plan moyen $P(A)$ est égale à 6. C7 est dans ce plan dont N8 est éloigné de 1,417 (9) Å. Les angles de torsion C1—C7—N8—C9 et C1—C7—N8—C11 valent respectivement 61 (1) et −58 (1)°. Le plan défini par C7—N8—C10 [plan $P(B)$] et celui du cycle benzénique sont orthogonaux, l'angle dièdre $P(A)P(B)$ ayant une valeur de 90,7 (6)°.

Dans la chaîne dodécylammonium les longueurs des liaisons C—N, celles des liaisons C—C et les angles C—C—C ont des valeurs moyennes respective-

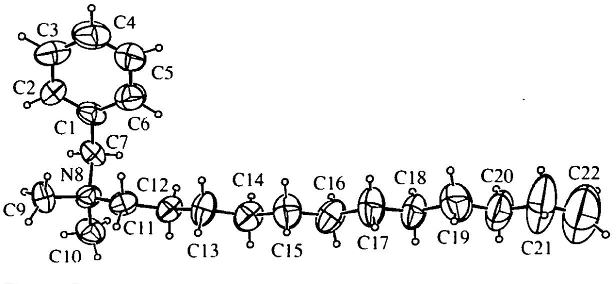


Fig. 1. Dessin de la molécule indiquant le numéro des atomes. Les ellipsoïdes de vibration des atomes ont une probabilité de 50%.

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