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Structure of 1,5,6-Trimethylbicyclo[2.2.1]hepta-2,5-diene-2,3-dicarbonitrile, $C_{12}H_{12}N_2$

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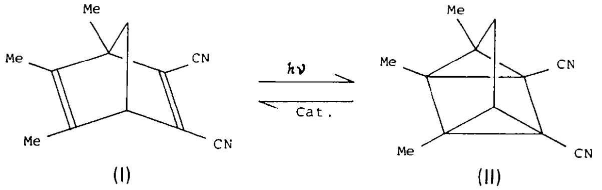
Abstract. $M_r = 184{\cdot}24$, monoclinic, $P2_1/n$, $a = 16{\cdot}033$ (4), $b = 9{\cdot}509$ (1), $c = 7{\cdot}012$ (1) Å, $\beta = 92{\cdot}11$ (1)°, $V = 1068{\cdot}4$ (3) Å^3, $Z = 4$, $D_x = 1{\cdot}145$, $D_m = 1{\cdot}145$ Mg m^{-3}, $F(000) = 392$, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu(\text{Mo } K\alpha) = 0{\cdot}075$ mm^{-1}. The structure was solved by a symbolic addition procedure and refined to a final R value of 0·055 for 1778 observed reflexions. All C—C—C angles in the norbornadiene nucleus are less than the tetrahedral value, indicating considerable strain in the skeleton; the average value of the angles at the double bonds is 107·3 (5)°. The bridgehead angle is 93·6 (2)°.

Introduction. Previously, one of us (Yoshida, 1981) reported the characteristic photophysicochemical properties of donor–acceptor norbornadienes, such as their large light sensitivity in the visible spectral region and their photo-valence isomerization with high quantum yield close to unity even in the presence of oxygen.



To obtain a structural basis for the properties, the molecular structure of the title compound [DTBH, (I)] was determined by X-ray crystallography.

Experimental. A prismatic pale-yellow crystal of DTBH crystallized from benzene solution, 0·25 × 0·28 × 0·39 mm, sealed in a glass capillary tube, density measured in an aqueous KI solution by flotation, systematic absences: $h0l$, $h + l = 2n + 1$; $0k0$, $k = 2n + 1$, indicating space group $P2_1/n$, Rigaku automated four-circle diffractometer, graphite-monochromated Mo $K\alpha$; unit-cell parameters determined from 25 reflexions by least squares, ω–2θ scan method, scan speed 8° min^{-1} in 2θ, scan range 2·0° + 0·7° tan θ, backgrounds counted for 10s on either side of peak, five reference reflexions (004, 440, 511, $\bar{4}\bar{4}0$ and $00\bar{4}$) measured every 50 reflexions showed intensity fluctuations less than 6%; within range $2\theta < 55°$ 1778 intensities with $|F_o| > 2\sigma(|F_o|)$ measured, $h = -20$ to 20, $k = 0$ to 12, $l = 0$ to 9, intensities corrected for Lorentz and polarization factors, but not for absorption; structure solved by a symbolic addition procedure, and refined by a block-diagonal least-squares method with anisotropic temperature factors for the non-H atoms, H atoms from difference Fourier map included in refinement with isotropic temperature factors; function minimized $\sum w(|F_o| - |F_c|)^2$; $w = 1{\cdot}0$ for $0 < |F_o| < 12{\cdot}5$, $w = (12{\cdot}5/|F_o|)^2$ for $|F_o| > 12{\cdot}5$; final $R = 0{\cdot}055$, $R_w = 0{\cdot}066$, maximum shifts in final refinement cycle for non-H and H atoms $0{\cdot}1\sigma$ and $0{\cdot}3\sigma$ respectively, maximum and minimum heights in final difference Fourier map $\pm 0{\cdot}14$ e Å^{-3}; atomic scattering factors from *International Tables for X-ray Crystallography* (1974), computations carried out at the Okayama University Computer Center; programs used were *SIGM, TANG, HBLS*-V and *DAPH* (Ashida, 1973), *MOLCON* (Fujii, 1979) and *DCMS*3 (Takenaka, 1977).

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Discussion. The final atomic positional parameters and isotropic temperature factors are in Table 1.* Fig. 1 shows the molecular structure and the thermal ellipsoids. Table 2 lists the bond lengths and angles. A table containing selected best planes, deviations of atoms from them and dihedral angles has been deposited.* The C—C single bonds all have normal length, the mean distance being 1·542 (4) Å; the C=C bond lengths average 1·330 (3) Å, in agreement with the corresponding values in norbornadiene (Morino, Kuchitsu & Yokozeki, 1967). These facts indicate that the introduction of the electron-donating and accepting groups to norbornadiene does not affect the molecular dimensions in the crystalline state. The C≡N bond lengths compare well with the value found in tetracyano-*p*-quinodimethane salts (Langer, Huml & Reck, 1982). The C(5)—C(11) and C(6)—C(12) lengths (1·490 and 1·497 Å, respectively) are slightly shorter than the value expected for a C(sp^2)—C(sp^3) length of 1·52 Å.

All the C—C—C angles in the norbornadiene nucleus [the C(1)—C(7)—C(4) angle in particular] are less than the tetrahedral value, indicating considerable strain in the skeleton; the average value of the angles at the double bonds is 107·3 (5)°. The bridgehead angle C(1)—C(7)—C(4) is 93·6 (2)°.

All the intermolecular separations < 4·0 Å were calculated, and those less than 3·8 Å are listed in Table 3. A stereoview showing the molecular packing is given in Fig. 2. The intermolecular distances are in the expected range for non-bonding contacts.

1,5,6-Trimethylquadricyclane-2,3-dicarbonitrile (II) is orthorhombic with $a = 13{\cdot}95$, $b = 7{\cdot}064$, $c = 10{\cdot}71$ Å and space group $P2_12_12_1$, $Z = 4$. The crystal structure analysis of this compound is now in progress.

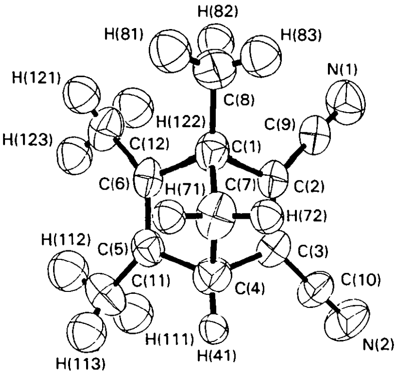

Fig. 1. Perspective view of the molecule with the atom-numbering scheme. Thermal ellipsoids are drawn at the 50% probability level.

Table 1. *Fractional atomic coordinates* (× 10^4) *of non-*H *atoms and equivalent isotropic temperature factors* (Å^2) *with e.s.d.'s in parentheses*

$B_{eq} = \frac{4}{3}(\beta_{11}a^2 + \beta_{22}b^2 + \beta_{33}c^2 + 2\beta_{13}ac\cos\beta)$ (Hamilton, 1959).

	x	*y*	*z*	B_{eq}
N(1)	6025 (1)	611 (3)	2425 (3)	6·29 (7)
N(2)	4015 (2)	−2605 (2)	2045 (4)	6·60 (7)
C(1)	4034 (1)	2470 (2)	2767 (3)	3·69 (5)
C(2)	4448 (1)	1011 (2)	2581 (3)	3·55 (5)
C(3)	3842 (1)	52 (2)	2485 (3)	3·78 (5)
C(4)	3012 (1)	855 (2)	2593 (3)	4·12 (5)
C(5)	2932 (1)	1739 (2)	756 (3)	3·83 (5)
C(6)	3538 (1)	2691 (2)	853 (3)	3·62 (5)
C(7)	3309 (1)	2001 (2)	4009 (3)	4·36 (5)
C(8)	4596 (2)	3646 (3)	3479 (4)	5·43 (7)
C(9)	5321 (1)	774 (2)	2479 (3)	4·15 (5)
C(10)	3939 (1)	−1421 (2)	2236 (3)	4·56 (6)
C(11)	2314 (1)	1401 (3)	−814 (4)	5·58 (7)
C(12)	3799 (2)	3734 (3)	−605 (4)	5·38 (7)

Table 2. *Interatomic distances and angles involving non-hydrogen atoms*

(i) Bond lengths (Å)

C(1)—C(2)	1·546 (3)	C(1)—C(8)	1·510 (3)
C(1)—C(6)	1·546 (3)	C(2)—C(9)	1·422 (3)
C(1)—C(7)	1·544 (3)	C(3)—C(10)	1·421 (3)
C(2)—C(3)	1·332 (3)	C(5)—C(11)	1·490 (4)
C(3)—C(4)	1·539 (3)	C(6)—C(12)	1·497 (3)
C(4)—C(5)	1·539 (3)	C(9)—N(1)	1·142 (3)
C(4)—C(7)	1·539 (3)	C(10)—N(2)	1·140 (3)
C(5)—C(6)	1·327 (3)		

(ii) Bond angles (°)

C(2)—C(1)—C(6)	104·9 (2)	C(2)—C(1)—(8)	116·1 (2)
C(2)—C(1)—C(7)	97·1 (2)	C(6)—C(1)—C(8)	117·9 (2)
C(6)—C(1)—C(7)	98·8 (2)	C(7)—C(1)—C(8)	118·7 (2)
C(1)—C(2)—C(3)	107·7 (2)	C(1)—C(2)—C(9)	124·9 (2)
C(2)—C(3)—C(4)	106·8 (2)	C(3)—C(2)—C(9)	127·3 (2)
C(3)—C(4)—C(5)	105·9 (2)	C(2)—C(3)—C(10)	126·7 (2)
C(3)—C(4)—C(7)	97·8 (2)	C(4)—C(3)—C(10)	126·4 (2)
C(5)—C(4)—C(7)	99·6 (2)	C(4)—C(5)—C(11)	122·2 (2)
C(4)—C(5)—C(6)	106·8 (2)	C(6)—C(5)—C(11)	130·8 (2)
C(1)—C(6)—C(5)	107·8 (2)	C(1)—C(6)—C(12)	122·4 (2)
C(1)—C(7)—C(4)	93·6 (2)	C(5)—C(6)—C(12)	129·6 (2)
		N(1)—C(9)—C(2)	178·4 (2)
		N(2)—C(10)—C(3)	179·6 (3)

(iii) Non-bonding intramolecular contacts (Å)

C(1)—C(3)	2·327 (3)	C(8)—C(12)	3·094 (4)
C(1)—C(5)	2·325 (3)	C(9)—C(10)	3·044 (3)
C(2)—C(4)	2·308 (3)	C(11)—C(12)	3·254 (4)
C(2)—C(6)	2·452 (3)		
C(2)—C(7)	2·315 (3)		
C(3)—C(5)	2·458 (3)		
C(3)—C(7)	2·319 (3)		
C(4)—C(6)	2·306 (3)		
C(5)—C(7)	2·351 (3)		
C(6)· C(7)	2·347 (3)		

Table 3. *Intermolecular contacts* (Å) *less than* 3·8 Å *involving non-hydrogen atoms*

$N(1)\cdots C(11^{i})$	3·699 (4)	$C(5)\cdots N(2^{iii})$	3·587 (3)
$N(1)\cdots N(2^{ii})$	3·662 (4)	$C(5)\cdots C(10^{iii})$	3·789 (3)
$N(1)\cdots C(5^{i})$	3·611 (3)	$C(7)\cdots N(2^{iii})$	3·790 (4)
$N(1)\cdots C(10^{ii})$	3·360 (3)	$C(11)\cdots N(2^{iii})$	3·582 (4)
$N(1)\cdots C(11^{ii})$	3·501 (4)	$N(1)\cdots C(3^{iv})$	3·623 (3)
$C(3)\cdots N(1^{ii})$	3·514 (3)	$N(1)\cdots C(7^{iv})$	3·656 (3)
$C(9)\cdots C(10^{ii})$	3·607 (3)	$C(8)\cdots C(8^{v})$	3·557 (5)
$C(4)\cdots N(2^{iii})$	3·582 (4)		

Symmetry code: none *x*,*y*,*z*; (i) $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$; (ii) $1 - x, -y, -z$; (iii) $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$; (iv) $1 - x, -y, 1 - z$; (v) $1 - x, 1 - y, 1 - z$.

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* Lists of structure factors, anisotropic temperature factors, coordinates of the H atoms, bond lengths and angles involving H atoms, and details of least-squares planes, deviations of atoms from them and dihedral angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38644 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

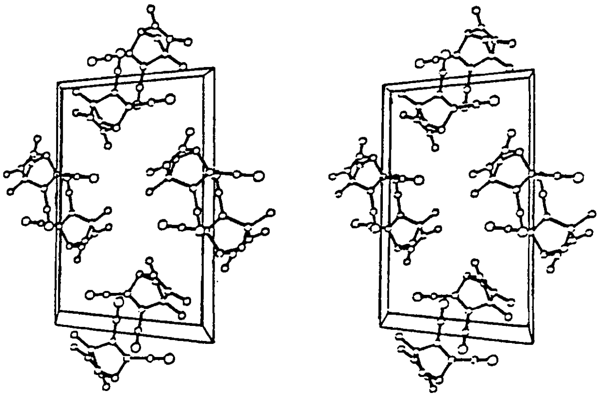

Fig. 2. Stereoview of the packing of the molecules. The origin is at the lower left-hand corner, **a** is vertical, **b** is horizontal and **c** towards the viewer.

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Structure of the Melampolide Sesquiterpene Lactone Alloschkuhriolide, $C_{15}H_{18}O_4$

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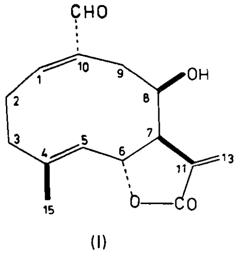
Abstract. $M_r = 262 \cdot 3$, orthorhombic, $P2_12_12_1$, $a = 5 \cdot 7993$ (6), $b = 14 \cdot 945$ (1), $c = 15 \cdot 730$ (2) Å, $U = 1363 \cdot 3$ (3) Å^3, $Z = 4$, $D_m = 1 \cdot 26$, $D_x = 1 \cdot 28$ Mg m^{-3}, Cu $K\alpha$, $\lambda = 1 \cdot 54184$ Å, $\mu = 0 \cdot 67$ mm^{-1}, $F(000) = 560$, $T = 295$ K, $R = 0 \cdot 058$ for 1049 observed reflections. Alloschkuhriolide (I) is the C(6), C(7) *trans*-fused product of relactonization of schkuhriolide (II), a naturally occurring C(7),C(8) *cis*-fused sesquiterpene lactone. The relactonization does not alter the gross conformation of the cyclodecadiene skeleton. It seems, however, that it results in a certain release of strain in the molecule.

Introduction. Recently we have reported the crystal structure of schkuhriolide monohydrate, a naturally occurring sesquiterpene lactone of the melampolide type, which is exceptional among melampolides in possessing a *cis* lactone ring closed at C(8) (Rychlewska, 1982). Comparison of this structure with other melampolides studied by X-ray methods has revealed considerable conformational similarity in these compounds. The conformation of the ten-membered ring in melampolides seemed to be mainly determined by the *cis, trans* nature of the double bonds within the ring. It was, therefore, of interest to learn the extent to which the γ-lactone orientation affects the ten-membered-ring conformation. Our previous results showed that relactonization of a 7,8-*cis*-lactonized melampolide to a 6,7-*trans*-lactonized compound proceeds without much conformational change within the molecule. As a complementary study we have undertaken an X-ray analysis of alloschkuhriolide (I), which is the product of schkuhriolide (II) relactonization upon strong alkaline treatment and subsequent acidification (Samek, Holub, Błoszyk & Drożdż, 1979).



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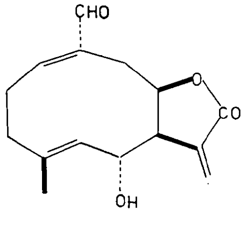

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