Acta Cryst. (1989). C**45**, 1803–1805

Structures of (*E*,*E*)-1,1′-Ethanediylidenebis(2,3-dihydro-1*H*-indene), (*E*,*E*)-1,1′-Ethanediylidenebis(1,2,3,4-tetrahydronaphthalene) and (*E*,*E*)-5,5′-Ethanediylidenebis(6,7,8,9-tetrahydro-5*H*-benzocycloheptene)

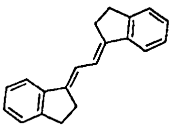
By Patrick J. Carroll, John N. Haseltine, Robin M. Hochstrasser and Amos B. Smith, III*

Department of Chemistry and Laboratory for Research on the Structure of Matter,
University of Pennsylvania, Philadelphia, PA 19104, *USA*

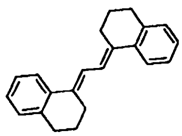
(*Received* 20 *October* 1988; *accepted* 21 *March* 1989)

Abstract. $C_{20}H_{18}$, $M_r = 258{\cdot}37$, monoclinic, $P2_1/c$, $a = 5{\cdot}359\,(1)$, $b = 14{\cdot}392\,(2)$, $c = 9{\cdot}112\,(2)$ Å, $\beta = 90{\cdot}16\,(1)°$, $V = 702{\cdot}8$ Å^3, $Z = 2$, $D_x = 1{\cdot}221$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 0{\cdot}64$ cm^{-1}, $F(000) = 276$, $T = 297$ K, final $R = 0{\cdot}056$ for 1114 unique observed reflections. $C_{22}H_{22}$, $M_r = 286{\cdot}42$, monoclinic, $P2_1/c$, $a = 4{\cdot}668\,(1)$, $b = 11{\cdot}220\,(2)$, $c = 15{\cdot}115\,(2)$ Å, $\beta = 90{\cdot}89\,(1)°$, $V = 791{\cdot}6$ Å^3, $Z = 2$, $D_x = 1{\cdot}202$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 0{\cdot}63$ cm^{-1}, $F(000) = 308$, $T = 297$ K, final $R = 0{\cdot}052$ for 1297 unique observed reflections. $C_{24}H_{26}$, $M_r = 314{\cdot}47$, monoclinic, $P2_1/c$, $a = 11{\cdot}667\,(1)$, $b = 6{\cdot}610\,(1)$, $c = 12{\cdot}720\,(2)$ Å, $\beta = 114{\cdot}85\,(1)°$, $V = 890{\cdot}1$ Å^3, $Z = 2$, $D_x = 1{\cdot}173$ g cm^{-3}, λ(Cu $K\alpha$) = 1·54184 Å, $\mu = 4{\cdot}58$ cm^{-1}, $F(000) = 340$, $T = 297$ K, final $R = 0{\cdot}071$ for 1219 unique observed reflections. The X-ray structure determinations confirmed the (*E*,*E*)-configurations of the double bonds in the title compounds.

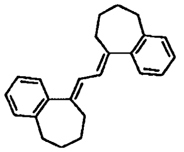
Introduction. The title compounds [(1)–(3)] were prepared as part of a study of the photoisomerization processes of stilbene and diphenylbutadiene (Lee, Bain, Han, McCarthy, Haseltine, Smith & Hochstrasser, 1986; Lee, Haseltine, Smith & Hochstrasser, 1988). Crystallographic structure determinations were undertaken to define unambiguously the geometric configurations of the trisubstituted double bonds in each of the hydrocarbons.



(1)



(2)



(3)

Experimental. Data collected on Enraf–Nonius CAD-4 diffractometer. Table 1 lists data collection parameters for the three title compounds [(1)–(3)]. Intensities of standard reflections measured every 3500 s of X-ray exposure showed no significant decay. Data corrected for Lorentz and polarization effects but not for absorption. Structure solved by *MULTAN*11/82 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982). Each of the molecules was found to lie on a crystallographic center of symmetry with the midpoint of the central σ-bond on the symmetry center. H atoms found from subsequent difference Fourier syntheses. Refinement by full-matrix least squares to minimize $\sum w(|F_o| - |F_c|)^2$ with $w = 1/\sigma^2(F_o)$ where $\sigma(F_o) = \sigma(F_o^2)/2F$ and $\sigma(F_o^2)$ was estimated from counting statistics. Non-H atoms refined anisotropically; H-atom positions were refined; H-atom thermal parameters were fixed at 6·0 Å^2. Atomic scattering

Table 1. *Data collection parameters*

	(1)	(2)	(3)
Crystal size (mm)	0·34 × 0·20 × 0·12	0·42 × 0·26 × 0·08	0·27 × 0·16 × 0·08
Reflections for lattice parameters:	25	25	25
No. and 2θ range (°)	17–27	12–27	25–60
No. of reflections measured	1762	2131	1928
hkl ranges	±6, +18, +11	+6, +14, ±19	±14, +8, +15
Radiation, λ (Å)	Mo $K\alpha$ 0·71073	Mo $K\alpha$ 0·71073	Cu $K\alpha$ 1·54184
2θ range (°)	4–55	4–55	6–140
No. of observed reflections [$F_o^2 > 3\sigma(F_o^2)$]	1114	1297	1219
No. of variables	118	133	148
Max. LS shift to e.s.d. ratio	0·03	0·04	0·06
Residual electron density (e Å^{-3})	0·42	0·36	0·54
R	0·056	0·052	0·071
wR	0·070	0·069	0·077
S	1·89	1·78	2·03

---

* To whom all correspondence should be addressed.

0108-2701/89/111803-03$03.00

factors from Cromer & Waber (1974); anomalous-dispersion terms from Ibers & Hamilton (1964). All computer programs from Enraf–Nonius *Structure Determination Package* (Frenz, 1978).

Table 2. *Positional parameters for compounds* (1), (2) *and* (3)

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

	x	y	z	B_{eq}(Å^2)
(1)				
C(1)	1·0040 (3)	0·4501 (1)	0·0032 (2)	3·51 (3)
C(2)	0·8545 (3)	0·3969 (1)	0·0867 (2)	3·25 (3)
C(3)	0·6494 (4)	0·4309 (1)	0·1883 (2)	4·03 (4)
C(4)	0·5270 (4)	0·3433 (1)	0·2531 (2)	3·93 (4)
C(5)	0·6707 (3)	0·2635 (1)	0·1886 (2)	3·40 (3)
C(6)	0·6420 (4)	0·1690 (1)	0·2133 (2)	4·30 (4)
C(7)	0·7998 (4)	0·1069 (1)	0·1454 (2)	4·64 (5)
C(8)	0·9870 (4)	0·1382 (1)	0·0523 (3)	4·65 (4)
C(9)	1·0163 (4)	0·2322 (1)	0·0253 (2)	4·21 (4)
C(10)	0·8571 (3)	0·2952 (1)	0·0940 (2)	3·24 (3)
H(1)	1·126 (5)	0·418 (2)	−0·057 (3)	6·0*
H(3)	0·738 (5)	0·470 (2)	0·266 (3)	6·0*
H(3′)	0·523 (5)	0·467 (2)	0·130 (3)	6·0*
H(4)	0·544 (5)	0·343 (2)	0·364 (3)	6·0*
H(4′)	0·355 (5)	0·341 (2)	0·221 (3)	6·0*
H(6)	0·512 (5)	0·146 (2)	0·280 (3)	6·0*
H(7)	0·778 (5)	0·043 (2)	0·163 (3)	6·0*
H(8)	1·094 (5)	0·093 (2)	0·006 (3)	6·0*
H(9)	1·154 (4)	0·252 (2)	−0.042 (3)	6·0*
(2)				
C(1)	0·4450 (4)	0·0303 (2)	0·4611 (1)	3·77 (3)
C(2)	0·4932 (3)	0·1457 (1)	0·4402 (1)	3·35 (3)
C(3)	0·6822 (4)	0·2225 (2)	0·4993 (1)	4·24 (4)
C(4)	0·6385 (4)	0·3548 (2)	0·4840 (1)	4·61 (4)
C(5)	0·6780 (4)	0·3838 (2)	0·3870 (1)	4·34 (4)
C(6)	0·4711 (3)	0·3130 (2)	0·3306 (1)	3·57 (3)
C(7)	0·3690 (4)	0·3609 (2)	0·2512 (1)	4·37 (4)
C(8)	0·1793 (4)	0·2996 (2)	0·1978 (1)	5·01 (4)
C(9)	0·0812 (4)	0·1894 (2)	0·2245 (1)	4·86 (4)
C(10)	0·1779 (4)	0·1403 (2)	0·3032 (1)	4·16 (4)
C(11)	0·3788 (3)	0·1993 (1)	0·3577 (1)	3·30 (3)
H(1)	0·331 (5)	−0·017 (2)	0·421 (2)	6·0*
H(3)	0·909 (5)	0·202 (2)	0·488 (2)	6·0*
H(3′)	0·639 (5)	0·203 (2)	0·563 (2)	6·0*
H(4)	0·779 (5)	0·402 (2)	0·521 (2)	6·0*
H(4′)	0·429 (5)	0·376 (2)	0·503 (2)	6·0*
H(5)	0·888 (5)	0·364 (2)	0·369 (2)	6·0*
H(5′)	0·647 (5)	0·473 (2)	0·379 (2)	6·0*
H(7)	0·444 (5)	0·445 (2)	0·236 (2)	6·0*
H(8)	0·112 (5)	0·337 (2)	0·143 (2)	6·0*
H(9)	−0·060 (5)	0·146 (2)	0·191 (2)	6·0*
H(10)	0·098 (5)	0·061 (2)	0·322 (2)	6·0*
(3)				
C(1)	0·9452 (3)	−0·0486 (6)	0·9554 (3)	4·21 (8)
C(2)	0·8486 (3)	0·0482 (5)	0·8697 (2)	3·82 (7)
C(3)	0·8365 (3)	0·2729 (6)	0·8546 (3)	4·58 (9)
C(4)	0·8636 (4)	0·3565 (6)	0·7533 (3)	5·4 (1)
C(5)	0·7655 (3)	0·2886 (6)	0·6337 (3)	5·09 (9)
C(6)	0·7651 (3)	0·0627 (6)	0·6120 (3)	4·70 (8)
C(7)	0·6988 (3)	−0·0666 (5)	0·6674 (2)	3·82 (7)
C(8)	0·5974 (3)	−0·1868 (6)	0·6003 (3)	4·30 (8)
C(9)	0·5357 (3)	−0·3127 (6)	0·6459 (3)	4·77 (9)
C(10)	0·5780 (3)	−0·3223 (6)	0·7674 (3)	4·71 (9)
C(11)	0·6789 (3)	−0·2047 (6)	0·8344 (3)	4·33 (8)
C(12)	0·7416 (3)	−0·0762 (5)	0·7903 (2)	3·73 (7)
H(1)	0·942 (4)	−0·206 (7)	0·961 (3)	6·0*
H(3)	0·908 (4)	0·349 (7)	0·930 (3)	6·0*
H(3′)	0·739 (4)	0·317 (7)	0·832 (3)	6·0*
H(4)	0·961 (4)	0·304 (7)	0·773 (3)	6·0*
H(4′)	0·869 (4)	0·518 (7)	0·761 (3)	6·0*
H(5)	0·794 (4)	0·370 (7)	0·577 (3)	6.0*
H(5′)	0·671 (4)	0·339 (7)	0·623 (3)	6·0*
H(6)	0·871 (4)	0·016 (7)	0·642 (3)	6·0*
H(6′)	0·718 (4)	0·032 (7)	0·526 (3)	6·0*
H(8)	0·564 (3)	−0·170 (7)	0·509 (3)	6·0*
H(9)	0·457 (4)	−0·405 (7)	0·597 (3)	6·0*
H(10)	0·528 (4)	−0·428 (7)	0·798 (3)	6·0*
H(11)	0·712 (4)	−0·207 (7)	0·922 (3)	6·0*

*Thermal parameters of starred atoms were not refined.

Discussion. Final positional and equivalent isotropic thermal parameters are listed in Table 2.* *ORTEP* (Johnson, 1965) drawings of the molecules appear in Fig. 1.

All three molecules exhibit some delocalization of the exocyclic double bond. Thus, in (1), the

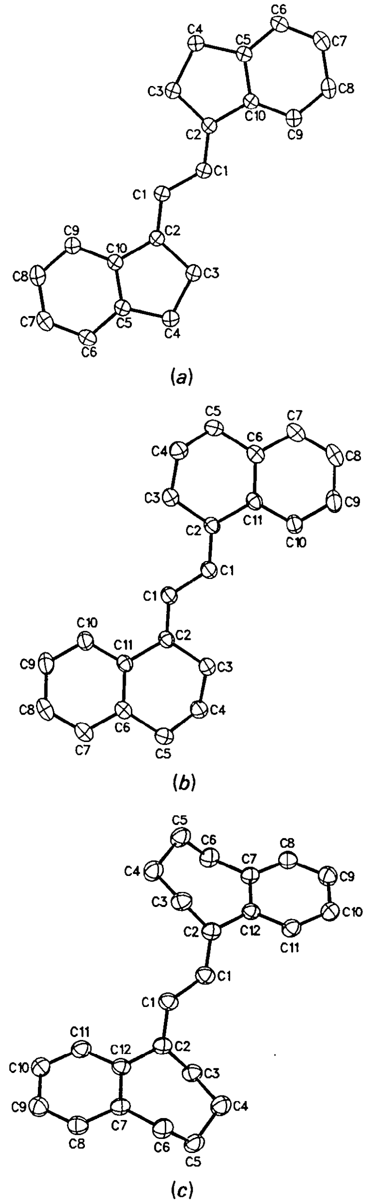


Fig. 1. *ORTEP* drawings of the title compounds: (*a*) (1), (*b*) (2) and (*c*) (3) (30% probability thermal ellipsoids).

---

* Tables of anisotropic thermal parameters, bond distances, bond angles and observed and calculated structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52055 (25 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

C(1)—C(1) bond, 1·438 (2) Å, and the C(2)—C(10) bond, 1·465 (2) Å, are shortened (compared to the sum of single-bond covalent radii for carbon, 1·544 Å, Pauling, 1960). Likewise, in (2), the C(1)—C(1) bond, 1·446 (2) Å, and the C(2)—C(11) bond, 1·477 (2) Å, are shortened; and in (3), the C(1)—C(1) bond, 1·454 (4) Å, and the C(2)—C(12) bond, 1·481 (4) Å, are shortened. There is, however, only a slight lengthening of the C(1)—C(2) double bond: in (1), 1·345 (2) Å; in (2), 1·353 Å; and in (3), 1·355 (4) Å (the sum of double-bond covalent radii for carbon is 1·334 Å).

In (1), the cyclopentene ring is planar within 0·008 Å. In (2), the cyclohexene ring is not planar, with C(4) 0·69 Å out of the plane of C(2), C(3), C(5), C(6) and C(11).

This research was supported by the National Science Foundation, Laboratory for Research on the Structure of Matter (LRSM), Grant No. DMR-85-19059.

References

CROMER, D. T. & WABER, J. T. (1974). In *International Tables for X-ray Crystallography*, Vol. IV, Table 2.2A. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

FRENZ, B. A. (1978). *The Enraf-Nonius CAD-4 SDP – A Real-Time System for Concurrent X-ray Data Collection and Crystal Structure Solution*. In *Computing in Crystallography*, edited by H. SCHENK, R. OLTHOF-HAZEKAMP, H. VAN KONINGSVELD & G. C. BASSI, pp. 64–71. Delft Univ. Press.

IBERS, J. A. & HAMILTON, W. C. (1964). *Acta Cryst.* **17**, 781–782.

JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.

LEE, M., BAIN, A. J., HAN, C. H., MCCARTHY, P. J., HASELTINE, J. N., SMITH, A. B. III & HOCHSTRASSER, R. M. (1986). *J. Chem. Phys.* **85**, 4341.

LEE, M., HASELTINE, J. N., SMITH, A. B. III & HOCHSTRASSER, R. M. (1989). *J. Am. Chem. Soc.* **111**, 5044.

MAIN, P., FISKE, S. J., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1982). *MULTAN*11/82. *A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.

PAULING, L. (1960). *The Nature of the Chemical Bond*, 3rd ed., p. 224. Ithaca: Cornell Univ. Press,

---

Acta Cryst. (1989). C**45**, 1805–1808

Structure of Dimethyl (1*S*,3*S*)-1-Methoxycarbonylmethyl-1,2,3,4-tetrahydro-9*H*-pyrido[3,4-*b*]indole-1,3-dicarboxylate at 165 K

BY JUDITH H. EVERETT, COLIN D. REYNOLDS AND CATHERINE A. SPARKS

Structural Biophysics Unit, School of Information Science and Technology, Liverpool Polytechnic, Liverpool L3 3AF, England

WALTER PANGBORN AND PHYLLIS STRONG

Department of Molecular Biophysics, Medical Foundation of Buffalo Inc., 73 High Street, Buffalo, NY 14203, USA

AND PATRICK D. BAILEY, ZBIGNIEW DAUTER, MADELEINE HELLIWELL AND SEAN P. HOLLINSHEAD

Department of Chemistry, University of York, Heslington, York YO1 5DD, England

(*Received* 15 *December* 1988; *accepted* 29 *March* 1989)

Abstract. $C_{18}H_{20}N_2O_6$, $M_r = 360·4$, orthorhombic, $P2_12_12_1$, $a = 11·999$ (1), $b = 13·693$ (1), $c = 10·612$ (1) Å, $V = 1743·6$ (2) Å^3, $Z = 4$, $D_x = 1·37$ Mg m^{-3}, λ(Cu $K\alpha$) = 1·5418 Å, $\mu = 0·83$ mm^{-1}, $F(000) = 712$, $T = 165$ (1) K, $R = 0·028$, $wR = 0·033$ for 1362 observed reflections. The CO_2Me and CH_2CO_2Me groups attached to C(3) and C(5) are both equatorial and the CO_2Me group at C(3) is axial. The six-membered heterocyclic ring is in a half-chair conformation. The crystal packing is determined by an intermolecular hydrogen bond between N(1) and O(52) [N···O = 2·857 (3) Å] and by several short contacts involving the carbonyl O atoms of the substituents at C(3) and C(5).

Introduction. The tetrahydro-β-carboline moiety occurs in many indole alkaloids, and the assignment of stereochemistry to these systems is often a crucial step in the structure elucidation of natural products of this type. The synthesis of these compounds also