Crystal Structure of *syn*-2,2′-Bifenchylidene E at −120 °C

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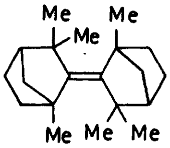
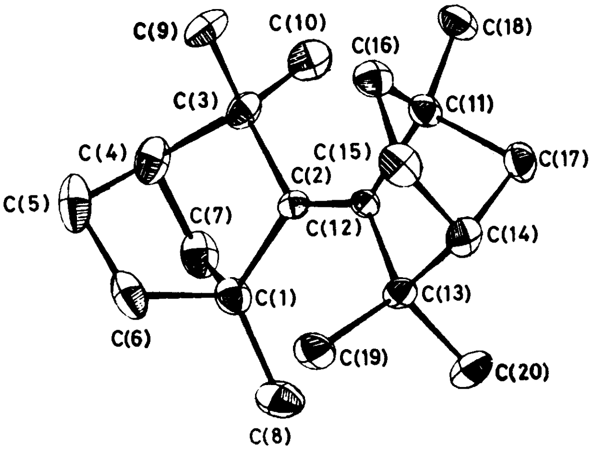
An *X*-ray crystal structure determination at −120 °C of *syn*-2,2′-bifenchylidene E, (I) [orthorhombic, space group $P2_12_12_1$, a = 8.574(2), b = 9.568(2), c = 19.841(3) Å, Z = 4, direct methods, final R 0.050 for 2 129 independent reflexions] shows the effects of steric hindrance on bond distances, valence angles, and twist of the central double bond. Mean $C(sp^2)$–$C(sp^3)$ single-bond distance is 1.565 Å, while the spread of $C(sp^3)$–$C(sp^3)$(Me) distances is 1.512—1.555 Å. Central bond-lengthening due to steric hindrance is not very apparent (1.349 Å). Valency-angle distortions relieve steric hindrance in methyl groups. The shortest 1,6-intramolecular contact between methyl group carbons is 3.145 Å. Intermolecular contacts are as expected.



(I)



Numbering of carbon skeleton and thermal ellipsoids drawn at a probability 0.40

THE synthesis of *syn*-2,2′-bifenchylidene E, (I), together with other very hindered olefins has been accomplished recently *via* the addition of a diazo-compound to a thione and subsequent extrusion of nitrogen and sulphur.[1-3] It was expected[4] that strong steric hindrance would deform the central $C(sp^2)$=$C(sp^2)$ system, as in 1,1-diphenyl-2,2-di-t-butylethylene (II).[5] It was also of interest to know which of the four possible conformational isomers[4] had been obtained, and a crystal-structure determination was therefore carried out by use of direct methods (SIG2, SYMBAD, TANFOR).[6] Atomic co-ordinates for carbon and hydrogen atoms are listed in Table 1, and the Figure[7] shows the carbon

TABLE 1

Atom co-ordinates (C × 10^4, H × 10^3) with estimated standard deviations in parentheses

	x	*y*	*z*
C(1)	2 675(3)	4 187(2)	3 991(1)
C(2)	1 496(2)	5 403(2)	3 875(1)
C(3)	271(3)	5 207(2)	4 454(1)
C(4)	1 039(3)	4 024(3)	4 872(1)
C(5)	2 569(4)	4 507(3)	5 206(1)
C(6)	3 682(4)	4 626(3)	4 608(1)
C(7)	1 624(4)	3 070(3)	4 333(1)
C(8)	3 557(3)	3 507(3)	3 419(2)
C(9)	11(3)	6 487(3)	4 897(1)
C(10)	−1 330(3)	4 628(3)	4 214(1)
C(11)	370(2)	7 669(2)	3 319(1)
C(12)	1 562(2)	6 465(2)	3 430(1)
C(13)	2 956(2)	6 872(2)	2 949(1)
C(14)	2 445(3)	8 342(3)	2 706(1)
C(15)	2 414(3)	9 418(2)	3 279(1)
C(16)	1 005(3)	8 959(2)	3 701(1)
C(17)	726(3)	8 123(3)	2 592(1)
C(18)	−1 384(3)	7 426(3)	3 383(1)
C(19)	4 552(3)	6 959(3)	3 291(1)
C(20)	3 096(3)	5 951(3)	2 315(1)
H(4)	35(3)	362(3)	520(1)
H(5A)	286(3)	380(3)	554(1)
H(5B)	247(4)	542(3)	546(2)
H(6A)	448(3)	406(3)	468(1)
H(6B)	407(3)	554(3)	452(1)
H(7A)	218(3)	232(3)	448(1)
H(7B)	82(3)	269(2)	404(1)
H(8A)	444(4)	421(4)	325(1)
H(8B)	281(3)	327(3)	304(1)
H(8C)	411(3)	266(3)	363(1)
H(9A)	−68(3)	729(3)	468(1)
H(9B)	−35(4)	622(3)	531(1)
H(9C)	94(3)	686(2)	503(1)
H(10A)	−182(5)	501(4)	386(2)
H(10B)	−177(5)	417(4)	455(2)
H(10C)	−127(5)	361(5)	408(2)
H(14)	301(3)	869(2)	237(1)
H(15A)	230(3)	1 031(3)	307(1)
H(15B)	333(3)	942(3)	356(1)
H(16A)	32(3)	962(3)	371(1)
H(16B)	125(3)	876(3)	416(1)
H(17A)	16(3)	897(2)	246(1)
H(17B)	52(2)	746(2)	225(1)
H(18A)	−169(3)	730(2)	383(1)
H(18B)	−167(3)	666(3)	311(1)
H(18C)	−196(3)	827(2)	318(1)
H(19A)	505(3)	605(3)	337(1)
H(19B)	521(3)	743(3)	301(1)
H(19C)	455(4)	757(3)	370(1)
H(20A)	353(4)	507(3)	241(1)
H(20B)	372(4)	643(3)	198(1)
H(20C)	215(3)	593(3)	207(1)

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skeleton of the molecule together with the atom numbering systems used. C–C Bond lengths are listed in Table 2, C–C–C bond angles in Table 3. The positions of hydrogen atoms were well resolved except for those bonded to C(10), which had the greatest B values, but we preferred not to exclude these from the F_c calculation.

TABLE 2

C–C bond lengths (Å) *

C(2)–C(3)	1.568	C(12)–C(13)	1.522
C(3)–C(10)	1.555	C(13)–C(19)	1.530
C(3)–C(9)	1.523	C(13)–C(20)	1.540
C(3)–C(4)	1.556	C(13)–C(14)	1.551
C(4)–C(5)	1.537	C(14)–C(17)	1.506
C(4)–C(7)	1.500	C(17)–C(11)	1.537
C(5)–C(6)	1.528	C(11)–C(18)	1.527
C(6)–C(1)	1.555	C(11)–C(16)	1.547
C(1)–C(7)	1.554		
C(1)–C(8)	1.512	C(15)–C(16)	1.534
C(1)–C(2)	1.558	C(15)–C(12)	1.556
C(2)–C(12)	1.349	C(15)–C(14)	1.534

* Estimated standard deviations 0.004 Å.

TABLE 3

Bond angles (°) *

C(1)–C(2)–C(12)	129.2	C(11)–C(12)–C(2)	128.6
C(3)–C(2)–C(12)	126.8	C(13)–C(12)–C(2)	127.9
C(1)–C(2)–C(3)	103.7	C(11)–C(12)–C(13)	103.3
C(2)–C(1)–C(6)	106.0	C(12)–C(11)–C(16)	106.9
C(2)–C(1)–C(7)	101.7	C(12)–C(11)–C(17)	102.2
C(2)–C(1)–C(8)	122.4	C(12)–C(11)–C(18)	121.5
C(6)–C(1)–C(7)	99.5	C(16)–C(11)–C(17)	99.5
C(6)–C(1)–C(8)	115.4	C(16)–C(11)–C(18)	115.3
C(7)–C(1)–C(8)	108.8	C(17)–C(11)–C(18)	108.5
C(1)–C(6)–C(5)	104.2	C(11)–C(16)–C(15)	103.8
C(4)–C(5)–C(6)	103.0	C(14)–C(15)–C(16)	103.1
C(3)–C(4)–C(5)	111.8	C(13)–C(14)–C(15)	112.5
C(3)–C(4)–C(7)	101.3	C(13)–C(14)–C(17)	101.3
C(5)–C(4)–C(7)	101.7	C(15)–C(14)–C(17)	100.8
C(2)–C(3)–C(4)	101.5	C(12)–C(13)–C(14)	101.4
C(2)–C(3)–C(9)	115.1	C(12)–C(13)–C(19)	115.1
C(2)–C(3)–C(10)	114.2	C(12)–C(13)–C(20)	114.3
C(4)–C(3)–C(9)	109.6	C(14)–C(13)–C(19)	110.0
C(4)–C(3)–C(10)	106.2	C(14)–C(13)–C(20)	106.7
C(9)–C(3)–C(10)	109.5	C(19)–C(13)–C(20)	108.9
C(1)–C(7)–C(4)	95.1	C(11)–C(17)–C(14)	95.4

* Estimated standard deviations 0.2° for C–C–C angles.

The molecular overcrowding does not reflect strongly on the central double-bond distance [1.349 Å *vs.* commonly accepted values 1.337 ± 0.006,[8] and 1.335 ± 0.010 Å (ref. 9)]. Even the deviation from planarity of the central $C(sp^2)$–$C(sp^2)$ system is small: the dihedral angle between the planes through atoms C(1)—(3) and C(11)—(13) corresponds to a twist of the double bond by 11.8° *vs.* 24° in (II). Steric hindrance causes a more obvious lengthening in $C(sp^2)$–$C(sp^3)$ bond lengths, the mean of these being 1.565 Å, *vs.* the more usual value [9] of 1.501 Å. At the same time the angles $C(sp^2)$–$C(sp^3)$–$C(sp^3)$(Me) are greatly enlarged with respect to the tetrahedral angle. The angles involving C(8) and C(18), mean 122°, are particularly large, while for the other four methyl groups the same angles have a mean of 114.7°. This difference is not surprising because both C(8) and C(18) are each pushed by two methyl groups, and conversely the ' push ' of each single methyl group is absorbed by two others. This fact also explains why the ethylenic system is closer to C_{2v} than to *mmm* symmetry. Notice that while atoms C(1), C(2), C(11), and C(12) are strictly coplanar (±0.001 Å), atoms C(3) and C(13) are shifted out of this plane in the same direction by 0.16 Å.

Notwithstanding this deformation of the molecule there are some short to very short 1,6-intramolecular contacts (Table 4).

TABLE 4

Some short 1,6 Me · · · Me contacts (Å)

C(10) · · · C(18)	3.145	C(19) · · · C(8)	3.421
C(20) · · · C(8)	3.229	H(8A) · · · H(19A)	1.86
C(9) · · · C(18)	3.356	H(18A) · · · H(9A)	1.90

Assuming van der Waals radii of 1.7 for carbon and 1.2 for hydrogen,[10] the only intermolecular distance less than the sum of these radii is 2.29 Å for H(9A) · · · H(19C) at $-\frac{1}{2} + x, \frac{1}{2} + y, 1 - z$.

EXPERIMENTAL

syn-2,2′-Bifenchylidene E (I) (m.p. 126—127 °C) crystallizes in colourless and well-formed parallelopipeds which rapidly sublime. The study was undertaken at low temperature with the LT 1 apparatus of the Syntex $P\bar{1}$ diffractometer. Lattice parameters and intensities were obtained by maintaining the crystal in a flow of nitrogen at −120 °C. Lattice parameters were derived from a least-squares fit of 45 reflexions.

Crystal Data.—$C_{20}H_{32}$, $M = 272.5$. Orthorhombic, $a = 8.574(2)$, $b = 9.568(2)$, $c = 19.841(3)$ Å, $U = 1\,627.7$ Å^3, $D_c = 1.112$, $Z = 4$, $D_m = 1.074$ g cm^{-3} (at room temperature by flotation), $F(000) = 608$. Mo-K_α radiation, $\lambda = 0{,}710\,7$ Å, μ(Mo-K_α) = 0.7 cm^{-1}. Space group $P2_12_12_1$.

Collection of Intensities and Structure Determination.—Diffracted intensities were measured out to 2θ 55° by the θ—2θ scan technique, with variable scan-speed and graphite monochromated Mo-K_α radiation. Two standard reflexions monitored every 40 reflexions showed no significant change during data collection. In the explored range, 2 174 independent reflexions were measured, of which 2 129 had intensities above background. Intensities and their standard deviations were corrected for Lorentz and polarization effects but not for absorption.

TANFOR,[6] in the new multisolution version, gave 264 phases, which led to an E map from whose peaks the coordinates of all the carbon atoms were derived.

Structure Refinement.—Refinement on all 2 129 observed reflexions by a full-matrix least-squares process was by a modified version of ORFLS.[11] The function minimized was $w(\Delta F)^2$, with weights $w = 1/\sigma^2(F)$. Atomic scattering factors for carbon and hydrogen were taken from refs. 12

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and 13 respectively. After three cycles of isotropic refinement, a difference-Fourier map showed all hydrogen atom positions. In subsequent cycles, carbon atoms were accorded anisotropic and hydrogen atoms isotropic thermal parameters. Because of computer size limitation and the high number of parameters to be refined (309), hydrogen and carbon atoms were refined in separate cycles. As the highest shift in refined parameters was $<0.3\sigma$, refinement was considered complete. Final R values were 0.051 for all measured reflexions, 0.050 for 2 129 observed reflexions, while R' was 0.046 with a goodness-of-fit 1.30 $\{\Sigma w(\Delta F^2)/(n-p)]$, where n is the number of observations and p that of parameters$\}$. A final difference-Fourier synthesis, calculated on all observed reflexions, was in the range ± 0.25 eÅ^{-3}. Observed and calculated structure factors and atom thermal parameters are listed in Supplementary Publication No. SUP 22028 (14 pp., 1 microfiche).*

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* For details see Notice to Authors No. 7 in *J.C.S. Perkin II*, 1976, Index issue.

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