ether layer was washed with 10% hydrochloric acid and then with water, dried ($MgSO_4$), and concentrated[5c] to 8.9 g of crude product. The product was analyzed by high-pressure LC (silica column, methylene chloride) and GC/MS, and it was found to be a mixture (58:25:17) of alcohol **9**, ketone **4**, and unreacted ester **2b**. Alcohol **9** was separated from the mixture on a silica column by using methylene chloride as the eluant.

Dehydration of Alcohol 9. A mixture of alcohol **9** (4 g, 19.6 mmol and anhydrous copper(II) sulfate (0.75 molar equiv) was heated at 120 °C for 1 h.[13] The cooled mixture was diluted with ether, filtered through Dicalite, concentrated,[5c] and distilled [Kugelrohr, bp 92–95 °C (0.5 mm)] to give 3.5 g (96%) which was identified as a 29:71 mixture of alkenes represented by **10** as shown by GC/MS studies. Attempts to separate the alkenes by column chromatography (silica) or fractional distillation were unsuccessful. Anal. Calcd for $C_{14}H_{18}$ (mixture): C, 90.26; H, 9.74. Found: C, 90.39; H, 9.81.

1-Isopropyl-8-methyl-1,2,3,4-tetrahydronaphthalene (11a). A mixture of alkenes **10** (3.5 g, 18.8 mmol) was hydrogenated at 50 °C and 40 psi in 100 mL of acetic acid by using 700 mg of 5% Pd/C as described for **1** to give 3.2 g (91%) of hydrocarbon **11a** which was purified by elution through a column of silica with *n*-hexane and distillation [Kugelrohr, bp 82 °C (0.2 mm)]: ^1H NMR ($CDCl_3$) δ 6.95 (m, 3, Ar H), 2.27 (s, 3, Ar CH_3), 0.89 (d, 3, CH_3CH), 0.86 (d, 3, CH_3CH); ^{13}C NMR ($CDCl_3$) 140.01, 137.89, 135.54, 127.67, 126.33, and 124.87 (aromatic), 40.45, 31.02, 28.89, 23.99, 21.21, 19.90, 19.46, and 19.41 ppm (aliphatic); MS *m/e* (relative intensity) 188 (M^+, 4), 145 (100), 130 (6), 43 (5). Anal. Calcd for $C_{14}H_{20}$: C, 89.29; H, 10.71. Found: C, 89.05; H, 10.57.

1-Isopropyl-8-methylnaphthalene (12). A sample of 1.5 g (9 mmol) of hydrocarbon **11a**, 5 mL of cymene, and 150 mg of 10% Pd/C was refluxed for 55 h, cooled, filtered through Dicalite, concentrated[5c] under reduced pressure, and then dissolved in 15 mL of hot 95% ethanol containing 2.5 g of picric acid. When the mixture cooled, the picrate of **12** crystallized as orange needles. Filtration gave 3.2 g or product, mp 108–109 °C. The picrate was decomposed on a column of basic alumina by using *n*-hexane[20] to give 0.9 g (60%) of **12**: bp 104–105 °C (Kugelrohr, 0.1 mm); ^1H NMR ($CDCl_3$) δ 7.65–7.10 (m, 6, Ar H), 4.12 (m, 1, CH_3CH); ^{13}C NMR ($CDCl_3$) 146.28, 135.46, 133.65, 131.58, 130.20, 128.16, 127.56, 124.75, 124.37, 123.61, 29.67, 26.18, 25.15 ppm (×2); MS *m/e* (relative intensity) 184 (M^+, 74), 169 (100), 154 (72), 141 (45), 115 (35), 83 (56), 76 (50). Anal. Calcd for $C_{14}H_{16}$: C, 91.25; H, 8.75. Found: C, 91.41; H, 8.65.

Acknowledgment. We thank the U.S. Department of Energy, Bartlesville Energy Technology Center, for support through Contracts DE-AC19-80BC-10298 and DE-AS19-80BC-10307.

Registry No. 1, 518-86-5; **2a**, 81603-28-3; **2a** acid chloride, 81603-45-4; **2b**, 81603-29-4; **3**, 81603-30-7; **4**, 81603-31-8; **5**, 67757-66-8; **5** 2,4-DNP, 81603-32-9; **6a**, 81603-33-0; **6b**, 81603-34-1; **7**, 61886-71-3; **7** picrate, 81603-35-2; **8a**, 81603-36-3; **8b**, 81603-37-4; **9**, 81603-38-5; **10** (isomer 1), 81603-39-6; **10** (isomer 2), 81603-40-9; **10** (isomer 3), 81603-41-0; **11a**, 81603-42-1; **11b**, 81603-43-2; **12**, 81603-44-3; **13a**, 19310-98-6; **13b**, 15724-49-9; 1-ethyl-7-methylnaphthalene, 31032-92-5; 1-methylnaphthalene, 90-12-0; methyl bromide, 74-83-9.

Identification of Configurational Isomers of Some 3,3′-Disubstituted 1,1′-Biindans and Related Compounds

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rac- and *meso*-3,3′-biindan-1-ones have been prepared for the first time and the configuration of the former has been identified by X-ray diffraction analysis. The configuration of the following compounds were then related to these two diastereomers by unambiguous syntheses: *rac*- and *meso*-3,3′-biindan-1-ol, two isomers of *rac*-3,3′-dichloro-1,1′-biindan, two isomers of *rac*-3,3′-dibromo-1,1′-biindan, *rac*-1,1′-biindan, *rac*-1,1′-bi-1*H*-indene, and one racemic pair of 1-(1-indanyl)-2-indene. All, but the last three (whose configurations were previously unknown) are new compounds.

The configurations of several 1,1′-biindans and 1,1′-bi-1*H*-indene were required for a research project. Only one form each of the known 1,1′-biindan (1)[1] and 1,1′-bi-1*H*-indene (2)[2] have been reported, but as far as we can determine, the configurations were never identified. The other desired compounds (3–6) were never reported in the literature.

rac-3,3′-Biindan-1-one (3) was prepared for the first time and its configuration was identified unequivocally by X-ray diffraction analysis (Tables I and II and Figure 1). A second, lower melting isomer of 3 was assumed to be the meso form. The configurations of the other compounds reported in this paper were then related to these two diastereomers by chemical interconversion (outlined in Scheme I).

1,1′-Bi-1*H*-indene (2) was prepared by the usual method of coupling indenylmagnesium bromide in the presence of cupric chloride.[2] The product mixture, in a typical experiment, consisted of recovered indene (26%), crystalline 2 (mp 100 °C, 68%), and viscous oil. Gas and liquid chromatography of the oil revealed two components: one, with the greater retention time (volume), was identical with that of crystalline 2; the other component was assumed to be an isomer of 2 (mainly by comparison of the infrared and NMR spectra of the crystalline and oily samples).

Hydrochlorination[3] of crystalline 2 afforded two crystalline isomers of 3,3′-dichloro-1,1′-biindan (4): the first (mp 160–161 °C) in 76% yield and the second (mp 130–131 °C) in 17% yield. These same two isomers were obtained in reduced yields (30% and 17%, respectively) after hydrochlorination of an oily (mixed isomer) sample of 2. No other pure (crystalline) dichloro isomers could be obtained from the hydrochlorination of the oily or crystalline bi-

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(1) Anastassio, A. G.; Stelliff, F. L.; Griffin, G. U. *J. Org. Chem.* **1966**, *31*, 2705.

(2) Grignard, V.; Courtot, C. H. *C. R. Hebd. Seances Acad. Sci.* **1912**, *154*, 361; **1911**, *152*, 272. Panetta, C. A.; Bunce, S. C. *J. Org. Chem.* **1961**, *26*, 4860. Marechal, E.; Basselier, J. J.; Sigwalt, P. *Bull. Soc. Chim. Fr.* **1964**, 1740.

(3) Using the method of Pacand, R. C.; Allen, C. F. H. "Organic Syntheses"; Wiley: New York, 1943; Collect. Vol. II, p 336.

Table I. Experimental Data for the X-ray Diffraction Study of *rac*-3,3′-Biindan-1-one (*3*)

Crystal Parameters

space group $P2_12_12$
$V = 670.13$ Å^3
$a = 5.745$ (2) Å
$Z = 4$
$b = 19.313$ (8) Å
mol wt 262.31
$c = 6.040$ (2) Å
$d_{\text{calcd}} = 1.410$

Measurement of Intensity Data

radiation = Mo Kα ($\lambda = 0.709\,26$ Å)
monochromator = graphite
detector aperture = horizontal = $A + B \tan\theta$ ($A = 2.0$ mm, $B = 1.0$ mm)
rflctns measd = $(+)h,k,l$
max (2θ): 70.0°
scan type = ω, 2θ
scan speed = variable 0.08–0.4°/min
ω scan width = $0.54 + 0.35 \tan\theta$
background = moving crystal–moving counter, one fourth additional scan at the end of each scan
std rflctns = 3 measured every 280 reflections showed a negligible attenuation during the data collection
rflctns measured = 1747
data used ($F{*}F > 2.0\,\sigma\,(F{*}F)$) = 1062 rflctns

Table II. Atom Positions and Estimated Standard Deviations for *rac*-3,3′-Biindan-1-one (*3*)

atom	x/a	y/b	z/c
C1	0.5593 (3)	0.03590 (7)	0.5967 (3)
C2	0.7066 (3)	0.05021 (8)	0.7857 (3)
C3	0.5970 (3)	0.00066 (8)	0.9017 (3)
C4	0.4024 (3)	0.13578 (7)	0.7635 (3)
C5	0.2534 (4)	0.19197 (8)	0.7990 (3)
C6	0.0853 (3)	0.20581 (8)	0.6442 (3)
C7	0.0637 (3)	0.16448 (9)	0.4567 (3)
C8	0.2100 (4)	0.10840 (8)	0.4227 (3)
C9	0.3814 (3)	0.09419 (7)	0.5776 (3)
O10	0.6603 (3)	0.13579 (8)	0.0766 (3)
H1	0.660 (3)	0.0398 (8)	0.450 (3)
H2a	0.714 (4)	0.0127 (8)	0.886 (3)
H2b	0.858 (4)	0.0617 (11)	0.743 (3)
H5	0.264 (4)	0.2204 (9)	0.925 (4)
H6	−0.012 (5)	0.2447 (9)	0.660 (4)
H7	−0.052 (5)	0.1721 (10)	0.359 (4)
H8	0.187 (4)	0.0793 (7)	0.284 (4)

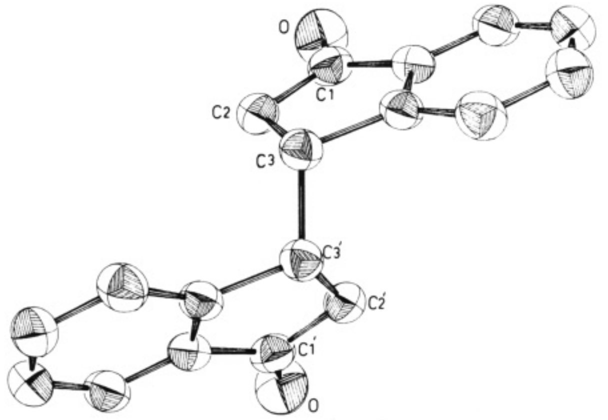


Figure 1. Perspective view of the molecular structure of *rac*-3,3′-biindan-1-one (**7**) as derived from X-ray diffraction analysis.

indenes. Unless inversion occurred during the addition of hydrogen chloride, the configurations of the 1- and 1′-positions of both crystalline isomers of **4** were identical with those of the same positions in crystalline **2**.

Theoretically, six 3,3′-dichloro isomers (three enantiomeric pairs, a, b, and c) are possible from the hydrochlorination of *rac*-1,1′-bi-1*H*-indene, while four isomers (one pair enantiomers, d, and two meso forms, e, f) may be obtained from *meso*-1,1′-bi-1*H*-indene (Chart I). In the absence of enantiomeric resolution, additions to each biindene leads to three diastereomers of the 3,3′-disubstituted 1,1′-biindane (such as **4** and **5**).

Scheme I

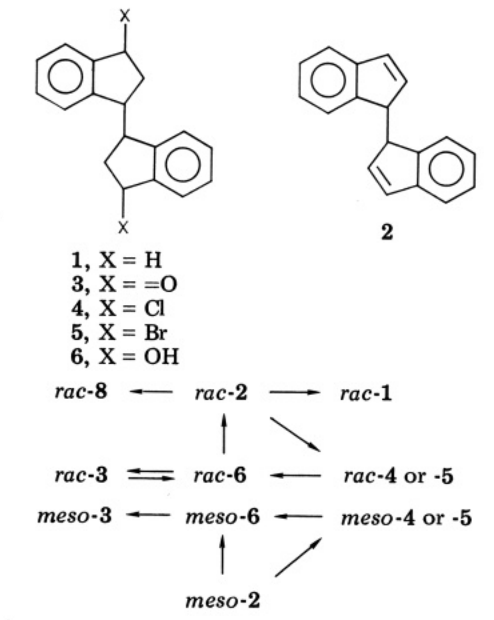
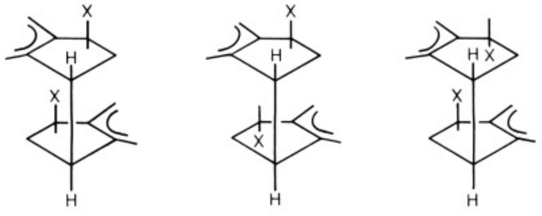


Chart I

Possible isomers resulting from addition of HX to *rac*-1,1′-bi-1*H*-indene (only one member of each enantiomeric pair shown):

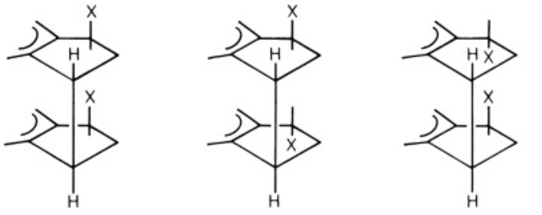


a
cis-trans

b
trans-trans

c
cis-cis

Possible isomers resulting from additions to *meso*-1,1′-bi-1*H*-indene:

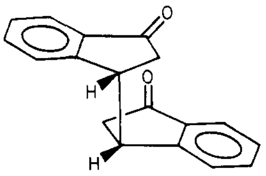


d
cis-trans (pair of enantiomers

e
trans-trans meso

f
cis-cis, meso

When either of the crystalline isomers of **4** was oxidized with chromic anhydride in aqueous acetic acid,[3] a diketone, **3** (mp 191–192 °C), was obtained in 87% yield. X-ray diffraction analysis of this isomer (NEH) showed it to be the racemic diastereomer with a skew conformation (**7**, Figure 1). Thus, each of the isolated crystalline isomers of **4** and the crystalline biïndene (**2**, mp 100 °C) must all be racemic with regard to the 1- and 1′-positions. The lower melting (130 °C) isomer of **4** was assigned the cis-trans configuration (a) on the basis that this was the only one of the three pertinent diastereomers that lacked C_2 symmetry: a characteristic supported by the relatively



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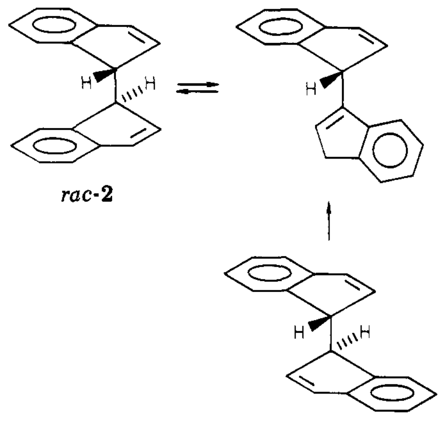
complex NMR spectra of the compound. The other crystalline isomer of **4** (mp 160 °C) showed a less complex spectrum and was either the trans-trans or cis-cis diastereomer (b or c, respectively).

rac-1,1′-Bi-1*H*-indene (**2**), (mp 100 °C) was hydrobrominated, and two of the three possible diastereomers of **5** were isolated: the first, mp 154–155 °C, in 82% yield and the second, mp 133–134 °C, in 13% yield. Like the dichloro isomers discussed above, the lower melting compound was devoid of C_2 symmetry (according to NMR spectra) and was assigned the cis-trans configuration (a). The major isomer must then have the trans-trans (b) or the cis-cis (c) configuration. When either of these samples of **5** were oxidized with chromic anhydride in aqueous acetic acid,[3] rac-3,3′-biindan-1-one was isolated in generally high (83–87%) yields. An oily sample of **2** (assumed to be composed of both the racemic and meso forms) was also hydrobrominated and the same two isomers (racemic a and b or c) were obtained in 65% and 9% yields, respectively. The filtrates from this experiment contained additional quantities of **5** that could not be crystallized. Since these oily samples of **5** (and similar ones of **4**) were probably composed of significant amounts of the elusive meso diastereomers, they were converted to the diketone **3** and diol **6** by oxidation with chromic anhydride followed by reduction with sodium borohydride. The diketone product was amorphous, but diol **6** crystallized readily from acetonitrile to afford two isomers: mp 188–189 °C, 86% from **5** and mp 175–176 °C, 11% from **5**. The higher melting isomer of **6** was identical with that obtained from the reduction of crystalline *rac*-3,3′-biindan-1-one (**3**). Its infrared spectrum showed evidence for intramolecular hydrogen bonds and the ^{1}H NMR spectrum was consistent with C_2 symmetry. Consequently, this isomer of **6** was assigned the racemic configuration, c (cis-cis). The second isomer (mp 175 °C) of diol **6** was oxidized to a crystalline diketone that was different (mp 161–162 °C) than but isomeric with the racemic diastereomer of **3**, previously isolated. This isomer therefore was assumed to be the meso form of diketone **3**, and the diol, which also showed intramolecular hydrogen bonding was assigned the meso configuration, **6f** (cis-cis). The hydrogen bond of **6c** was apparently stronger than that of **6f** according to the infrared absorption bands, which were found at 3480 and 3560 cm^{-1}, respectively. This evidence was consistent with the fact that intramolecular hydrogen bonds force the meso diol **6f** into a crowded conformation with the two aromatic rings eclipsed.

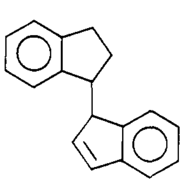
meso-3,3′-Biindan-1-ol (**6**) was then dehydrated under acidic conditions in an attempt to prepare a pure sample of *meso*-1,1′-bi-1*H*-indene (**2**). An oil, which resisted all attempts at crystallization, was obtained that proved to be a 76:24 mixture of *meso*- and *rac*-**2** according to ^{13}C NMR spectroscopy (80:20 by gas chromatography). A similar dehydration of pure *rac*-**6** afforded a 94% yield of an oily product that was 100% *rac*-**2** by gas and liquid chromatography. It crystallized in 75% yield (calculated from **6**). This evidence appears to support the greater stability of the racemic form of 1,1′-bi-1*H*-indene (**2**) compared to *meso*-**2**. Apparently, the latter diastereomer isomerizes to the former by migration of the double bond.



rac-**2**

meso-**2**

Pure *rac*-1,1′-bi-1*H*-indene (**2**) was hydrogenated to *rac*-1,1′-biindan (**1**) and *rac*-3,3′-dibromo-1,1′-biindan (**5b** or **5c**) afforded one of the racemic pairs of 1-(1-indanyl)-2-indene (**8**) after treatment with magnesium.



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Both products have been known for years.[1,4] However, their configurations were never reported.

Experimental Section

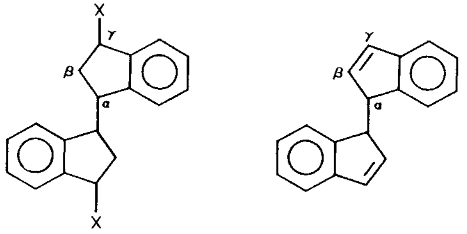
IR spectra were recorded on a Beckman Acculab 3 or Perkin-Elmer 521 spectrophotometer, ^{1}H NMR spectra on a Perkin-Elmer R-24B (60 MHz) or R-32 (90 MHz) spectrometer, and ^{13}C NMR spectra on a JEOL FX60Q instrument. Most of the spectral data are reported in Table III. Melting points are corrected and microanalyses were performed by the Analytical Department, Bristol Laboratories, Syracuse, NY. GC instruments used were the Hewlett-Packard Model 5840A and Perkin-Elmer Model Sigma 3B. The analytical HPLC instrument was a Waters Model ALC-100 with refractive index and ultraviolet detectors.

***rac*-1,1′-Bi-1*H*-indene (2).**[2] Ethylmagnesium bromide was prepared from 40 mL (58.4 g, 0.5 mol) of ethyl bromide and 12 g (0.5 mol) of magnesium turnings under an atmosphere of Ar. A solution of distilled indene (58.2 mL, 58.0 g, 0.5 mol) in 60 mL of dry toluene was added to the Grignard reagent during a 10-min period. The resultant yellow mixture was heated at the reflux temperature for 6 h.

A second flask was charged with 70 g (0.52 mol) of anhydrous $CuCl_2$[5] and 100 mL anhydrous ether and this was cooled to −5 °C under an Ar atmosphere. The above reaction mixture, which contained indenylmagnesium bromide, was added in one portion. The orange-red color changed to a black mixture, which was stirred at the above temperature for 6 h and then at room temperature for 8 h. It was filtered through Celite and the filter cake was washed with 500 mL of ether. The pale-yellow filtrate was washed with water (5 × 300 mL) and the organic solution was again filtered through Celite. The filtrate was dried (anhydrous $MgSO_4$), and the solvents were removed by distillation on a rotary evaporator under reduced pressure. The residual oil was distilled at 40 °C (1.0–2.0 torr) in order to separate 15 g of indene (26% recovery). The undistilled residual oil partially crystallized during overnight storage to a mixture (41 g) of red-yellow needles and an oil. This was separated into three portions and purified by preparative liquid chromatography on a Waters Prep 500 unit using 15% C_6H_6 and 85% 2,2,4-trimethylpentane and one silica column (V_r = 960, 1090 mL). Yellow needles (*rac*-**2**, 38.9 g, 68%) were obtained from either of the two fractions, which were recrystallized from hot C_2H_5OH: mp 99–100 °C (lit.[1,2] mp 99–100 °C).

Other runs afforded lower yields of crystalline *rac*-**2** and larger amounts of an oily product. The latter appeared to be a *mixture*

Table III. Melting Points and Spectral Data of the Disubstituted Biindans and 1,1′-Bi-1*H*-indenes



compd[a]	mp, °C	IR (KBr window), cm⁻¹)	^{1}H NMR[b,c] α	β	γ	aromatic	^{13}C NMR[b,c] α	β	γ	aromatic
rac-**2**	99–110	3070, 2870, 1700, 1455, 800, 760, 730, 720	4.16 (s)	5.75 (d)	6.65 (d)	7.3 (m)	51.1	144.3	145.6	121.1, 122.5, 124.7, 126.8, 131.8, 135.9
meso-**2**[d]	oil	3070, 2930, 2870, 1700, 1455, 790, 760, 735, 715 (neat)	4.11 (s)	6.3 (d)	6.7 (d)	7.3 (m)	50.7	136.7	144.9	121.0, 122.7, 124.6, 126.8, 128.2, 132.0
rac-**3**[e]	191–192	3420, 2920, 1700, 1590, 1460, 1285, 1270, 770, 775	4.1–4.3 (m)	1.6–2.7 (m)		7.3–7.9 (m)	40.7	37.8	204.5	123.9, 125.1, 128.2, 135.1, 137.5, 156.0
meso-**3**	161–162	3410, 2920, 1700, 1650, 1595, 1285, 760	4.0–4.2 (m)	2.0–3.0 (m)		6.8–7.8 (m)	41.5	40.0	204.6	123.8, 125.8, 128.4, 134.7, 138.2, 154.7
rac-**4b/c**	160–161	2980, 1475, 1460, 1240, 1225, 970, 940, 850, 760, 750, 730, 640, 625	4.3 (t)	1.6–2.1 (m)	5.41 (2 d)	7.3 (s)	43.6	38.3	61.8	124.0, 125.2, 127.7, 129.3, 143.4, 144.6
rac-**4a**	130–131	3020, 1450, 1440, 1305, 1215, 915, 845, 805, 790, 760, 750, 720, 620, 600	3.8–4.4 (m)	1.2–2.9 (m)	5.2–5.5 (m)	7.3 (s)	43.6, 44.5, 44.7	38.1, 38.3, 38.6	60.4, 62.0	123.8, 125.3, 127.7, 128.8, 129.1, 143.3, 143.7, 144.6
rac-**5b/c**	154–155	3020, 1470, 1450, 1190, 1140, 960, 845, 755, 745, 615	4.1–4.3 (m)	2.0–2.3 (m)	5.4–5.5 (2 d)	7.3 (s)	43.1	39.2	52.9	124.0, 125.3, 127.7, 129.2, 144.2, 144.7
rac-**5a**	133–134	2870, 1475, 1460, 1200, 845, 760, 745, 610	4.0–4.4 (m)	1.8–2.8 (m)	5.4–5.6 (m)	6.7–7.5 (m)	43.1, 44.0, 45.1	39.2, 41.2	52.9, 50.4	124.0, 124.4, 125.3, 125.4, 126.1, 127.7, 128.6, 129.0, 129.2, 144.2, 144.7
rac-**6c**	188–189	3300, 2870, 1465, 1330, 1090, 1055, 765, 755, 745	3.7 (m)	1.2–2.2 (m)	4.95 (m)	7.15 (m)[f]	42.3	37.0	72.7	123.4, 123.8, 126.3, 127.1, 143.7, 146.9[f]
meso-**6f**	175–176	3300, 3200, 2980, 2870, 1445, 1345, 1060, 1000, 770, 755, 735	3.5–3.7 (m)	1.3–1.7 (m)	4.9–5.2 (m)	6.8–7.4 (m)[f]	42.9	40.9	72.7	123.8, 126.3, 126.8, 143.2, 147.5[f]

[a] Satisfactory analytical data (±0.4% for C, H) for all new compounds except racemic-*3* were submitted for review. [b] Chemical shifts (δ) are reported in parts per million relative to $(CH_3)_4Si$ as an internal standard. [c] The solvent was $CDCl_3$. [d] Contaminated with some *Racemic-2*. [e] Anal. Calcd for $C_{18}H_{14}O_2$: C, 82.42; H, 5.37. Found: C, 81.99; H, 5.29. [f] In Me_2SO-d_6.

of biindene diastereomers (racemic and meso) after study of the pertinent spectra and analyses by gas or liquid chromatography. GC: 8-ft column packed with Gas Chrom Q silane-treated support coated with 11.85% w/w of OV-101 (methyl Silicone) stationary phase (Alltech Associates); 180 °C, isothermal, FID detector); retention times, 13.88 min for *rac*-**2** and 12.86 min for *meso*-**2**. Analytical LC: 0.8 × 10 cm, 10 μm, C18 reverse-phase Waters Radial-Pak cartridge, ambient temperature, ultraviolet detector; retention volumes for *meso*- and *rac*-**2**, 15.7 and 16.5 mL, respectively.

***rac*-3,3′-Dichloro-1,1′-biindans (4a and 4b or 4c).** Dry HCl was bubbled through a cold solution (5–10 °C) of 23 g (0.1 mol) of *rac*-1,1′-bi-1*H*-indene (**2**, mp 99–100 °C) in 100 mL of dry C_6H_6 during a 36-h period.[3] The progress of the reaction was monitored by TLC (E. Merck, silica gel 60 GF-254; hexane/EtOAc, 95:5). A white solid, which precipitated during the reaction period, was collected by filtration, washed with cold ether, and recrystallized from C_6H_6 to afford 17 g of crystals (**4b** or **4c**): mp 160–161 °C. The filtrate was concentrated under reduced pressure and the oily residue was crystallized from 50 mL of dry ether. A second crop of **4b/c** was obtained that weighed 6.1 g (76%, total yield of **4b/c**).

The remaining ethereal filtrate was stored at −5 °C for several days during which time 5.3 g (17%) of **4a** separated. It was recrystallized from hot C_6H_6: mp 130–131 °C.

***rac*-3,3′-Dibromo-1,1′-biindans (5a and 5b or 5c).** Anhydrous HBr was passed through a cold (5–10 °C) solution of 40 g (0.172 mol) of *rac*-1,1′-bi-1*H*-indene (**2**, mp 99–100 °C) in 200 mL of dry C_6H_6 during a 5-h period.[3] The progress of the reaction was monitored by TLC (E. Merck, silica gel 60 GF-254; hexane/EtOAc, 95:5). A yellow solid, which separated during this period, was filtered, washed with cold ether, and recrystallized from hot C_6H_6 to afford 30 g of white crystals of **5b/c**: mp 154–155 °C. A second crop of crystals was obtained by concentration of the filtrate under reduced pressure and addition of 50 mL of anhydrous ether to the residual oil. Crystals separated during storage and were also recrystallized from C_6H_6: weight, 23 g (total yield of **5b/c** was 82%).

The ethereal filtrate was stored at −5 °C for several days when 9.8 g (13%) of **5a** precipitated. It was recrystallized from C_6H_6: mp 133–134 °C.

***rac*-3,3′-Biindan-1-one (3).** To a warm (~45 °C), orange solution of 0.3 g (3.0 mmol) of CrO_3, 60 mL of glacial HOAc, and 5 mL of H_2O was added, in portions, 0.303 g (1.0 mmol) of *rac*-3,3′-dichloro-1,1′-biindan (**4a** or **4b/c**).[3] Successive portions were added as soon as the previous one dissolved. The dark-brown mixture was then stirred at 45–50 °C for 2 h. After cooling to room temperature, the mixture was diluted with 55 mL of water and neutralized with solid $NaHCO_3$. *rac*-**3** separated as a pink solid, which weighed 0.23 g (87%) and gave a positive (2,4-dinitrophenyl)hydrazine test. It was recrystallized from hot EtOH to afford a pale-pink product: mp 191–192 °C.

rac-3,3′-dibromo-1,1′-biindan (**5a** or **5b/c**) was also oxidized to *rac*-**3** by use of the procedure above. The yield was 83%.

X-ray Diffraction Analysis. Data Collection. A crystal of *rac*-3,3′-biindan-1-one (**3**) measuring 0.20 × 0.25 × 0.45 mm was mounted on the end of a thin glass fiber for the data collection. Diffraction data were collected at ambient temperature on an Enraf-Nonius CAD-4F automatic diffractometer using graphite monochromated Mo radiation. A unit cell was selected through the use of the search, centering, and indexing routines on 25 reflections with θ values out to 26°. The final unit cell parameters were determined to be $a = 5.745$ (2) Å, $b = 19.313$ (8) Å, $c = 6.040$ (2) Å, $\alpha = \beta = \gamma = 90°$. The cell dimensions and the observed systematic absences $h00$ ($h = 2n + 1$) and $0k0$ ($k = 2n + 1$) identified the unique orthorhombic space group $P2_12_12$. Three intense reflections were chosen as standard reflections and their intensities monitored during the data collection. These reflections showed no significant change in intensity during the data collection.

Solutions and Refinement. The structure was solved by examination of the E map calculated from the phase set with the highest Figure of Merit (MULTAN 78 program),[6] which revealed the location of all the unique nonhydrogen atoms. The structure refinement was carried out on a PDP 1134 computer using the Molecular Structure Corporation's SDP set of programs written by B. Frenz.[7] Full-matrix least-squares refinement was carried out in three stages. First, two cycles of refinement utilizing positional and isotropic thermal parameters for all unique atoms were done, and then the thermal factors were made anisotropic and two additional cycles of refinement using a variable weighting scheme were carried out. After the two cycles of refinement with anisotropic thermal parameters, the weighted and unweighted residuals were 0.093 and 0.084, respectively. The hydrogen atoms then were placed in their calculated positions and assigned isotropic thermal parameters, which were then refined along with the carbon and oxygen parameters. Three further cycles of full-matrix refinement gave weighted and unweighted residuals of 0.055 and 0.043 with an estimated standard deviation of an observation of unit weight of 1.56. During the last refinement cycle, the largest shift/error as 0.86. A difference Fourier map calculated on the basis of the atomic positions from the last refinement cycle gave no peaks as large as 0.15 electron/Å^3.

***rac*-3,3′-Biindan-1-ol (6c).** A solution of 0.2 g (5.2 mmol) of $NaBH_4$ in 10 mL of H_2O was added during a 5-min period to a stirred solution (15–18 °C) of 0.26 g (1.0 mmol) of *rac*-3,3′-biindan-1-one (**3**) in 150 mL of EtOH. The resultant mixture was then stirred in an ice bath for 15 min and at room temperature for 2 h. The EtOH was removed by distillation at reduced pressure and the residue was treated with 60 mL of cold 50% aqueous HCl. The solid product was collected by filtration and washed with H_2O. It was recrystallized from hot CH_3CN to afford 218 mg of white needles of **6c** (82%): mp 188–189 °C; IR (very dilute solution in CCl_4, cell pathlength 6 cm) 3615, 3600 (sharp, free OH stretching), 3480 cm^{-1} (br, intramolecular hydrogen-bonded OH stretching).

***meso*-3,3′-Biindan-1-ol (6f).** An oily sample of 3,3′-dibromo-1,1′-biindan (**5**) that was recovered from the filtrates of the crystalline racemic isomers (**5a** and **5b** or **5c**) was used in this experiment. It was assumed to consist, at least in part, of the meso diastereomer. This oil (3.9 g, 0.01 mol) was added in portions during a 1.0-h period to a stirred and warmed (45 °C) orange solution of 3.9 g (0.039 mol) of CrO_3, 130 mL of glacial HOAc, and 20 mL of H_2O. The resultant dark-brown mixture was heated at 45–50 °C for 2 h, after which it was cooled, diluted with 60 mL of H_2O, and neutralized by the addition of solid $NaHCO_3$. A green gummy product separated, collected, washed with water, and dried: 2.5 g. It resisted crystallization even after column chromatography. It was assigned the structure of 3,3′-biindan-1-one (**3**) mainly from an infrared band at 1700 cm^{-1}. A solution of this crude diketone (2.3 g, 8.7 mmol) in 200 mL of EtOH was cooled at 10 °C and then treated with a cold solution of 0.5 g (0.01 mol) of $NaBH_4$ in 10 mL of H_2O. The resultant red mixture was stirred cold for 15 min and at room temperature for 1 h. The EtOH was removed by distillation under reduced pressure and the residue was treated with 50 mL of cold 6 N HCl. The mixture was filtered and the collected solid was washed thoroughly with water and dried in order to afford 1.8 g of a pale-yellow powder. This was recrystallized from 15 mL of hot CH_3CN. Two crystalline forms precipitated: white needles, mp 188–189 °C, which were identical with those (**6c**) isolated earlier from the reduction of *rac*-3,3′-biindan-1-one, 1.5 g (86% from **5**), and pale yellow prisms, mp 175–176 °C, which were later shown to be *meso*-3,3′-biindan-1-ol (**6f**) by their oxidation to the meso diketone, 0.7 g (11% from **5**). Initially, these products could be separated by simply segregating them into two piles according to crystalline form. However, a more facile separation should be effected on the basis of the fact that the racemic isomer is soluble in EtOAc and the meso isomer is not. **6f**: IR (very dilute solution in CCl_4, cell pathlength, 6 cm) 3620, 3597 (free OH stretching),

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(4) Bergmann, E.; Taubadel, H. *Ber. Deutsch. Chem. Ges.* **1932**, *65*, 463.

(5) Anhydrous $CuCl_2$ was prepared by heating $CuCl_2{\cdot}2H_2O$ at 120 °C (20 torr) for 48 h.

(6) Main, P.; Hull, E. S.; Lessinger, L.; Germain, G.; Lecercq, J.-P.; Woolfson, M. M. "MULTAN 78, a System of Computer Programs for the Automatic Solution of Crystal Structures from X-Ray Diffraction Data"; Universities of York: England and Louvain, Belgium, 1978.

(7) Frenz, B. "SDP Enraf-Nonius Structure Determination Package", Version 16; Molecular Structure Corporation: College Station, TX, 1979.

3560 (intramolecular hydrogen-bonded OH stretching).

***meso*-3,3′-Biindan-1-one (3).** *meso*-3,3′-Biindan-1-ol (**6f**; 30 mg, 0.1 mmol) was added to a warmed (45 °C) and stirred mixture of 30 mg (0.3 mmol) of CrO_3, 20 mL of glacial HOAc, and 5 mL of H_2O. After 2 h of stirring at 45 °C, the mixture was cooled, diluted with 20 mL of H_2O, and neutralized with solid $NaHCO_3$. The green solution was extracted with EtOAc (5 × 50 mL) and the organic solution was washed with H_2O (3 × 50 mL) and dried over anhydrous $MgSO_4$. The solvent was removed by distillation under reduced pressure and the crystalline residue was 26 mg (88%) of *meso*-**3**, which was recrystallized from hot EtOH: mp 161-162 °C.

Dehydration of *meso*-6: Preparation of a Mixture of *rac*- and *meso*-1,1′-Bi-1*H*-indene (2). A mixutre of 100 mg (0.37 mmol) of *meso*-3,3′-biindan-1-ol (**6f**), 15 mL of dry C_6H_6, and 10 mg of *p*-toluenesulfonic acid monohydrate was heated at the reflux temperature for about 24 h. Water was collected in a Dean and Stark trap during this period. The mixture was washed with 5% aqueous $NaHCO_3$ (2 × 25 mL) and water (2 × 25 mL) and the benzene solution was dried over anhydrous Na_2SO_4. Distillation of the benzene at reduced pressure left 81 mg of an oily residue that resisted crystallization attempts. Gas chromatographic analysis (conditions given under preparation of *rac*-**2**, above) showed this oil to be a mixture of 80% *meso*- and 20% *rac*-**2**. Analysis of the C-1,1′ peaks in the ^{13}C NMR spectrum of this oil showed the isomer percentages to be 76% and 24%, respectively. The total yield of the oil was 95%.

When *rac*-3,3′-biindan-1-ol (**6c**) was dehydrated by the preceding procedure, a 94% yield of product was isolated that was 100% *rac*-**2** by gas chromatography. It readily solidified into yellow needles: mp 99-100 °C.

***rac*-1,1′-Biindan (1).** A solution of 0.5 g (2.1 mmol) of *rac*-1,1′-bi-1*H*-indene (**2**, mp 99-100 °C) and 18 mL of dry C_6H_6 was stirred with 1.0 g of 5% Pd-on-C, while H_2 (generated from 1.13 g of $NaBH_4$ and 20 mL of glacial HOAc) was passed through during a 2-h period. The mixture was filtered and the residue was washed with 100 mL of C_6H_6. The filtrate and washings were distilled under reduced pressure first to remove the solvent and then to purify the product, which weighed 0.5 g (100%): bp 180 °C (2 torr); UV (MeOH) λ_{max} 273.5 (ϵ 3.9), 267 (3.8), 260 (3.7) (identical with reported[1] values).

***rac*-1-(1-Indanyl)indene (8).** Active Mg was prepared by the following procedure.[8] To dried apparatus flushed with Ar were added 0.19 g (4.8 mmol) of freshly cut K, 50 mL of THF (distilled from sodium benzophenone ketyl and passed through a column of 10 g of Woelm neutral Al_2O_3, activity I), 0.25 g (2.6 mmol) of anhydrous $MgCl_2$, and 0.44 g (2.6 mmol) of anhydrous KI. This mixture was stirred and heated to the reflux temperature for 4 h during which time the active Mg separated as a fine black powder. *rac*-3,3′-Dibromo-1,1′-biindan (**5b/c**); 0.94 g, 2.3 mmol) was added to the above slurry of active Mg at room temperature. The resulting mixture was then heated to the reflux temperature under Ar for 24 h. The cooled mixture was diluted with Et_2O and filtered through Celite. The residue was washed with Et_2O. The filtrate and washings were combined and washed with water (3 × 100 mL), 5% aqueous sodium thiosulfate (3 × 100 mL), and 100 mL of brine. After drying, the organic phase was distilled under reduced pressure to afford 530 mg of a yellow oil. This was purified by preparative TLC (on a 2-mm layer of E. Merck silica gel F-254; hexane/EtOAc, 95:5) to yield 252 mg (47%) of 8: bp 110 °C (2 torr) [lit.[4] value bp 190 °C (12 torr)].

Also isolated from preparative TLC was 261 mg (49%) of *rac*-1,1′-bi-1*H*-indene (**2**): mp 98-101 °C.

If Mg turnings were used in the above procedure in place of the specially prepared active Mg, the yields of **8** and **2** were 44% and 25%, respectively. In this experiment, some starting material was recovered.

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Registry No. *rac*-**1**, 81523-13-9; *rac*-**2**, 81523-14-0; *meso*-**2**, 74339-76-7; *rac*-**3**, 81523-15-1; *meso*-**3**, 81523-16-2; *rac*-**4a**, 81523-17-3; *rac*-**4b**, 81571-00-8; *rac*-**4c**, 81571-01-9; *rac*-**5a**, 81523-18-4; *rac*-**5b**, 81571-02-0; *rac*-**5c**, 81571-03-1; *meso*-**5f**, 81571-04-2; *rac*-**6c**, 81523-19-5; *meso*-**6f**, 81571-05-3; *rac*-**8**, 81523-20-8; indene, 95-13-6.

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[8] Klabunde, K. J.; Efner, H. F.; Satek, L.; Donley, W. *J. Organomet. Chem.* **1974**, *71*, 309. Reike, R. D.; Hudnall, P. M. *J. Am. Chem. Soc.* **1972**, *94*, 7178. Reike, R. D.; Bales, S. E.; Hudnall, P. M.; Poindexter, G. S. *Org. Synth.* **1979**, *59*, 85.

A New Entry to the $C_{12}H_{12}$ Energy Surface: Pyrolysis and Photolysis of *trans*-β-[*anti*-9-Bicyclo[6.1.0]nona-2,4,6-trienyl]acrolein Tosylhydrazone Salts

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Thermal decomposition of the lithium salt of *trans*-β-[*anti*-9-bicyclo[6.1.0]nona-2,4,6-trienyl]acrolein tosylhydrazone (**8**) results in the formation of pentacyclo[$6.4.0.0^{2,12}.0^{3,7}.0^{4,11}$]dodeca-5,9-diene (**12**), *exo*- and *endo*-tricyclo[$4.4.2.0^{2,5}$]dodeca-3,7,9,11-tetraenes (**9** and **10**), 1,2-benzocycloocta-1,3,7-triene (**11**), and *syn*- and *anti*-9-(5-pyrazolyl)bicyclo[4.2.1]nona-2,4,7-trienes (**14** and **13**). The low-temperature photolysis of the sodium salt of tosylhydrazone **8** gives *anti*-9-(2-cyclopropen-1-yl)bicyclo[6.1.0]nona-2,4,6-triene (**20**), which affords pentacyclo[$6.4.0.0^{2,4}.0^{3,10}.0^{5,9}$]dodeca-6-11-diene (**22**) on thermolysis. Hydrocarbon **12** was formed in the photolysis of the sodium salt of *trans*-β-[*syn*-9-bicyclo[4.2.1]nona-2,4,7-trienyl]acrolein tosylhydrazone (**15**; available by thermal rearrangement of tosylhydrazone **8**) as the sole $C_{12}H_{12}$ product. Structure determinations and mechanistic investigations are discussed.

The isomeric $(CH)_{12}$ hydrocarbons present an interesting family of compounds because of the theoretical significance of many of the members and the varied electrocyclic and sigmatropic processes expected of the numerous valence tautomers. Despite these attractive features, chemical investigation in this area has been limited because of the relative unavailability of synthetic entries to these compounds. For these reasons, various research groups have