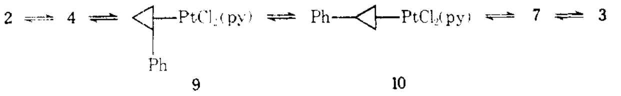
search. A generous load of platinum chloride by the Matthey-Bishop Co. is also gratefully acknowledged. The author would like to thank Professor J. Paukstelis for obtaining the NMR spectra, Professor H. Moser for assistance with the radioactive chloride experiment, and both them and Professor R. McDonald for helpful discussions. Partial support from the Department of Chemistry, Kansas State University, is also acknowledged.

Registry No.—**2**, 63469-62-5; **3**, 38889-63-3.

References and Notes

(1) (a) Zeise's dimer is di-μ-chloro-dichlorobis(η^2-ethene)diplatinum [12073-35-8]. (b) W. J. Irwin and F. J. McQuillin, *Tetrahedron Lett.*, 1937 (1968); F. J. McQuillin and K. G. Powell, *J. Chem. Soc., Dalton Trans.*, 2123 (1972).
(2) R. J. Puddephatt, M. A. Quyser, and C. F. H. Tipper, *J. Chem. Soc., Chem. Commun.*, 625 (1976).
(3) The ratio of **2/3** was 1:3 under these conditions.
(4) R. J. Al-Essa, R. J. Puddephatt, M. A. Quyser, and C. F. H. Tipper, *J. Organomet. Chem.*, **150**, 295 (1978).
(5) An alternate (olefin)metal-carbene mechanism has been discounted by Puddephatt[2] on the grounds that no styrene was found in the reaction when **2** was converted to **3**.
(6) P. W. Hall, R. J. Puddephatt, K. R. Seddon, and C. F. H. Tipper, *J. Organomet. Chem.*, **81**, 423 (1974).
(7) G. B. Kauffman, *Inorg. Synth.*, **7**, 249 (1963).
(8) The ratio of **2/3** in this experiment was ca. 1:2.5.
(9) Introduced as KCl. Chloride-38 has a half-life at 36 min. A sample was obtained from the Kansas State University reactor and was sufficiently active to be detected in the products.
(10) An alternate explanation could involve a pair of equilibrating edge complexes, **9** and **10**:



9 10

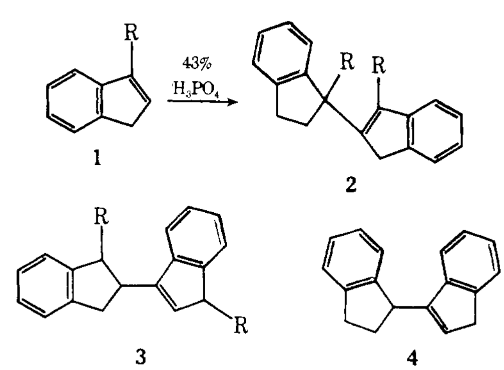
Diindene (Indene Dimer): A Triboluminescent Compound[1]

Wayland E. Noland,* Lawrence L. Landucci,[1a] and
James C. Darling[1b]

*School of Chemistry, University of Minnesota,
Minneapolis, Minnesota 55455*

Received October 10, 1978

Weissgerber[2] reported in 1911 the preparation of a dimer of 1*H*-indene (diindene) in nearly quantitative yield, a colorless solid, mp 51 °C (recrystallized from acetic acid), by refluxing 1*H*-indene with acetic or phosphoric acids. He suggested as possibilities two cyclobutane ([2 + 2]cycloadduct) structures. Stobbe and Färber[3] reported in 1924 that repetition of the preparation with phosphoric acid gave a colorless sample, mp 50–51 (solidified oil) and 57–58 °C (from acetic acid or ethanol, with a little water). The latter sample was converted to a dibromide, mp 120–121 °C, indicating that a double bond was present, and was oxidized with chromium(VI) oxide to 2,3-dihydro-1*H*-inden-1-one. On the basis of their evidence, they suggested possible structures **2a** and **3a**. Similarly, Marion[4] obtained from a sample of diindene recrystallized from ethanol, mp 55–56 °C, a dibromide, mp 126 °C. Stobbe and Färber[3] left open the question whether the lower melting solidified oil and the higher melting recrystallized sample were isomers or were the same compound in differing states of purity. The possibility of dimorphism does not seem to have been considered. The only appreciable difference they noted was that the lower melting form was autoxidized much more rapidly than the higher melting form. Dansi and Pasini,[5] who prepared their diindene with stronger acid (48% sulfuric acid), argued that at least two isomers were present since their diindene, when crystallized from ethanol or acetic acid, gave fractions having different and variable melting points. Furthermore, they obtained two different dibromides, mp 131–133 and 131–132 °C, and fractions of intermediate and depressed melting points, which were reported to be of different stability and formed in differing yields depending on which sample of diindene they were derived from. On the basis of this evidence they assigned structure **2a** to the lower melting diindene and suggested that the higher melting form was probably structure **4**. It should be noted, however, that **2a** could give rise to two diastereomeric dibromides. One, the trans, would be the result of normal anti addition of bromine to the double bond, and the other, the cis, could result from syn addition of bromine or from epimerization of a bromine at the benzyl (1) or tertiary (2) carbon atoms of the trans dibromide.



a, R = H; b, R = CH$_3$

In the present work indene was refluxed with 1:1 water–85% phosphoric acid according to the procedure of Weissgerber,[2] giving diindene in 77% yield as a colorless blue fluorescent oil, bp 158–161 °C (0.9 mm), which solidified on cooling to an extremely hard white crystalline solid, mp 42–52 °C. Two recrystallizations from acetic acid gave white needles, mp 59–60 °C. The NMR spectra of the two samples are the same, indicating that they are dimorphs, except for an impurity peak in the former at δ 0.98. Since the orientation of protonation and carbocation attack on the 1*H*-indene double bond would be expected to produce a benzyl cation, structure **2a** is more probable than **3a** (or **4**), a likelihood which was also recognized[6] before the acceptance of carbonium ion theory. The NMR spectra of diindene are consistent with structure **2a** since the indenyl vinyl proton and methylene group appear as broad singlets (in carbon tetrachloride) at δ 6.53 ($W_{1/2}$ = 3.5 Hz) and 3.21 ($W_{1/2}$ = 3 Hz), respectively, rather than being split by each other as would be expected for structures **3a** or **4**.

Dimerization of 3-methyl-1*H*-indene with phosphoric acid under corresponding conditions gave a dimer as a light yellow viscous oil, bp 162–166 °C (0.8 mm), $n^{25}{}_D$ 1.6088, having an NMR spectrum (in carbon tetrachloride) consistent with the corresponding structure **2b** (rather than **3b**) since there is no vinyl proton peak and the 2,3-dihydroindenyl methyl peak appears as a singlet at δ 1.52. The indenyl methyl absorption at δ 1.66 appears as a triplet ($J \approx 1.7$ Hz), however, apparently being involved in five-bond zigzag long range coupling[7] with the indenyl methylene group, whose absorption at δ 3.24 appears as an incompletely resolved quartet ($J \approx 1.7$, $W_{1/2}$ = 5.5 Hz).

The lower melting solidified form of diindene was markedly triboluminescent;[8] when broken, struck, or scratched vigorously it emitted flashes of blue light. The higher melting recrystallized form (white needles) was not triboluminescent under the same conditions. The surface of solidified diindene turns yellow on contact with air, apparently the result of autoxidation which can be retarded by storage in a brown bottle in a refrigerator. The yellow exterior (autoxidized material) is much more soluble in acetic acid than is diindene itself.

The blue triboluminescence observed with solidified diindene appears compatible with two of the types which have been reported: (1) the nitrogen gas discharge spectrum type of triboluminescence attributed to a piezoelectric effect in noncentrosymmetric crystals[8] observed with crystalline sugars such as sucrose[8,9] or with aniline hydrochloride[10,11] or (2) triboinduced photoluminescence (probably related to the blue fluorescence associated with the liquid) observed with aromatic compounds[11] such as resorcinol,[11] coumarin,[11,12] and phenanthrene.[11] We have not carried out the studies required to make a distinction. Also, we have not examined (but hope that others will) the structure of the easily formed autoxidation product(s) of solidified diindene, which may have its (their) origin in the same crystal strain which gives rise to triboluminescence in this form of the dimer.

Experimental Section

Diindene [2-(2,3-Dihydro-1*H*-inden-1-yl)-1*H*-indene] (2a). The general procedure is that of Weissgerber,[2] except that vigorous sitrring was used and the reflux time was increased from 15 to 23 h. 1*H*-Indene (>97.5% purity, 200 g, 1.68 mol) was added to a solution of 85% phosphoric acid (200 mL) in water (200 mL), and the resulting two-phase mixture was refluxed with vigorous stirring for 23 h. The progress of the dimerization was followed by comparison of the refractive index of the indene–diindene layer with synthetic mixtures of the two prepared as calibration standards. At 4 h the dimerization was 52% complete ($n^{24}{}_D$ 1.600), and at 23 h, when the reaction was terminated, it was 97.5% complete ($n^{24}{}_D$ 1.621). The pale yellow organic layer was separated, dried (KOH), and fractionally distilled, giving 1*H*-indene as a colorless forerun (8.85 g, 4% recovery), bp 30–35 °C (0.9 mm), $n^{24}{}_D$ 1.574, followed by diindene as a colorless but bright blue fluorescent (under UV light) liquid (156.0 g, 78%), bp 157–161 °C (0.9 mm), $n^{24}{}_D$ 1.622, which solidified after being kept at room temperature or in a refrigerator to an extremely hard white crystalline solid, mp 42–52 °C. The solid emitted flashes of blue light when broken, struck, or scratched vigorously with a spatula: literature nearly quantitative,[2] 55%;[6b] bp 154 (0.4 mm),[13] 160–165 (1 mm),[4] 177 (1 mm),[13] 145–160 (1–2 mm),[6c] 210 (12 mm),[6b] 235–245 (16 mm),[2] and 355 °C (755 mm);[13] $n^{20}{}_D$ 1.588;[14] mp 50–51,[3] 51,[2] and 53 °C.[6b] The NMR spectrum (in $CDCl_3$) was the same, except for an impurity peak at δ 0.98, as that reported (in CCl_4) below. Two recrystallizations from acetic acid gave white needles: mp 59–60 °C (lit. mp 55–56,[4] 56,[6c] 57–58,[3] and 57–59 °C[5]); UV (95% C_2H_5OH) λ_{max} nm (log ϵ) 224 sh (4.17), 259 (4.21), 263 sh (4.18), 269 sh (4.11), 272 sh (3.99), 282 sh (3.32), 288 sh (2.84); IR (CCl_4) cm^{-1} 1610 m (C=C); NMR (17% w/v, CCl_4) δ 2.22 (m, $W_{1/2}$ = 47.5 Hz, 2 H, CH_2), 2.90 (m, $W_{1/2}$ = 24 Hz, 2 H, CH_2), 3.21 (br s, $W_{1/2}$ = 3 Hz, 2 H, CH_2), 4.25 (t, J = 8 Hz, 1 H, CH), 6.53 (br s, $W_{1/2}$ = 3.5 Hz, 1 H, =CH), 7.12 (m, major peak at δ 7.08, $W_{1/2}$ = 25 Hz, 8 H, aromatic H).

Anal. Calcd for C_8H_{16} (232.31): C, 93.06; H, 6.94. Found: C, 92.96; H, 7.24.

3-Methylindene Dimer [3-Methyl-2-(2,3-dihydro-1-methyl-1*H*-inden-1-yl)-1*H*-indene] (2b). A mixture of 3-methyl-1*H*-indene (18.16 g, 139 mmol), 85% phosphoric acid (20 mL), and water (20 mL) was refluxed with vigorous stirring for 36 h. The progress of the dimerization was followed by rate of change of the refractive index of the monomer–dimer layer. When the dimerization appeared essentially complete (at 36 h), the yellow organic layer was separated, dried (KOH), and fractionally distilled, giving 3-methyl-1*H*-indene as a colorless forerun (2.07 g, 11% recovery), bp 40–49 °C (0.6 mm), $n^{25}{}_D$ 1.552, followed by dimer **2b** as a yellow viscous oil (7.93 g, 44%), bp 140–150 °C (0.6 mm), $n^{25}{}_D$ 1.6091. Redistillation of the product gave a viscous oil, collected in two fractions: (1) yellow (1.07 g, 6%), bp 156–162 °C (0.8 mm), $n^{25}{}_D$ 1.6078; and (2) light yellow (2.89 g, 16%), bp 162–166 °C (0.8 mm), $n^{25}{}_D$ 1.6088, which was used as an analytical sample; UV (95% C_2H_5OH) λ_{max} nm (log ϵ) 227 sh (3.84), 261 (4.04), 272 sh (3.90); IR (neat) cm^{-1} 1595 m (C=C); NMR (38% w/v, CCl_4) δ 1.30 (s, 0.4 H, impurity), 1.52 (s, 3 H, CH_3), 1.66 (t, J = 1.7 Hz, 3 H, CH_3), 2.22 (m, $W_{1/2}$ = 38 Hz, 2 H, CH_2), 2.83 (q, $J \approx$ 8 Hz, 2 H, CH_2), 3.24 (incompletely resolved q, J = 1.7 Hz, 2 H, CH_2), 7.11 (m, major peak at δ 7.07, $W_{1/2}$ = 26 Hz, 8 H, aromatic H).

Anal. Calcd for $C_{20}H_{20}$ (260.36): C, 92.26; H, 7.74. Found: C, 91.97; H, 8.36.

Acknowledgment. We are indebted to the following companies for support of summer fellowships to L.L.L.: (a) Monsanto Co., 1963; (b) E. I. duPont deNemours and Co., 1964; and (c) Procter and Gamble Co., 1965.

Registry No.—**1a,** 95-13-6; **1b,** 767-60-2; **2a,** 69381-18-6; **2b,** 69381-19-7.

References and Notes

(1) Taken from (a) in large part the Ph.D. Thesis of Lawrence L. Landucci, University of Minnesota, March 1967; *Diss. Abstr. B*, **28,** 3223–3224 (1968); and (b) the graduate research of James C. Darling, 1977–1978. (c) We are indebted to Mary Beth Seidlitz for an extensive literature review of triboluminescence.

(2) R. Weissgerber, *Ber. Dtsch. Chem. Ges.*, **44,** 1436–1448 (1911).

(3) H. Stobbe and E. Färber, *Ber. Dtsch. Chem. Ges.*, **57,** 1838–1851 (1924).

(4) L. Marion, *Can. J. Res., Sect. B*, **18,** 309–317 (1940).

(5) A. Dansi and C. Pasini, *Gazz. Chim. Ital.*, **81,** 507–510 (1951); *Chem. Abstr.*, **46,** 5563 (1952).

(6) (a) G. S. Whitby and M. Katz, *J. Am. Chem. Soc.*, **50,** 1160–1171 (1928); (b) E. Bergmann and H. Traubadel, *Ber. Dtsch. Chem. Ges. B*, **65,** 463–467 (1932); (c) J. Risi and D. Gauvin, *Can. J. Res., Sect. B*, **13,** 228–255 (1935).

(7) L. M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry", 2nd ed., Pergamon Press, Oxford, 1969, pp 333–334.

(8) A. J. Walton, *Adv. Phys.*, **26,** 887–948 (1977).

(9) J. I. Zink, G. E. Hardy, and J. E. Sutton, *J. Phys. Chem.*, **80,** 248–249 (1976).

(10) J. I. Zink, *Chem. Phys. Lett.*, **32,** 236–237 (1975).

(11) G. E. Hardy, J. C. Baldwin, J. I. Zink, W. C. Kaska, P.-H. Liu, and L. DuBois, *J. Am. Chem. Soc.*, **99,** 3552–3558 (1977).

(12) J. I. Zink and W. Klimt, *J. Am. Chem. Soc.*, **96,** 4690–4692 (1974).

(13) W. E. Sheehan, H. E. Kelly, and W. H. Carmody, *Ind. Eng. Chem.*, **29,** 576–579 (1937).

(14) Backcalculated from the reported[6c] values of $d^{20}{}_4$ 1.043 and $Mr^{20}{}_D$ 37.48 using the molecular weight of monomeric 1*H*-indene (116.15). The value calculated is quite different from what we observed.

Synthesis of 1,2-Disubstituted Acenaphthylenes

David A. Herold[1] and Reuben D. Rieke*[2]

Contribution from the William Rand Kenan, Jr.,
Laboratories of Chemistry, Department of Chemistry,
University of North Carolina, Chapel Hill, North Carolina 27514
and Department of Chemistry, University of Nebraska-Lincoln,
Lincoln, Nebraska 68588

Received August 28, 1978

Our initial interest in the synthesis of 1,2-disubstituted acenaphthylenes stemmed from our need to prepare acenaphthylene-1-diazonium-2-carboxylate (XII). This high energy compound (XII) should in theory thermally or photochemically decompose to form acenaphthyne, a benzyne analogue which had eluded the intensive efforts of Rasheed.[3] Subsequently, our interest in the photochemical investigation of four of these 1,2-disubstituted acenaphthylenes[4] was encouraged by the works of (1) Bouas-Laurent et al.[5] (photodimerization of monosubstituted CN and CO_2H acenaphthylenes), (2) Michl et al.[6] (photodimerization of 1,2-dibromoacenaphthylene and acenaphthylene to form the mixed dimer), and (3) Cowan and Drisko[7] (investigations of mechanisms and heavy atom effects in the dimerization of acenaphthylene). Additionally, several of these compounds have been studied by magnetic circular dichroism,[8] and the 1,2-dicyanoacenaphthylene has been studied by electron spin resonance.[9] The syntheses of nine of these compounds are herein reported.

Results and Discussion

The synthetic route planned for the diazonium carboxylate precursor (XI) is shown in Scheme I; the synthesis, a sequence of five steps initiated with acenaphthene, is a straightforward procedure with a sequence yield of 29%. The byproduct of this sequence of reactions and any compounds prepared from main sequence products are discussed along with their main se-

0022-3263/79/1944-1359$01.00/0 © 1979 American Chemical Society