# Synthesis of Bis(*as*-indacenyliron)

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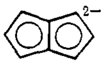
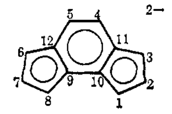
**Abstract:** The synthesis of bis(*as*-indacenyliron), the only compound known in which two metal atoms are sandwiched between a pair of aromatic rings, is described. Bis(*as*-indacenyliron) results when dilithium *as*-indacenide (II), formed in tetrahydrofuran by reaction of dihydro-*as*-indacene with *n*-butyllithium, is added to ferrous chloride. Photooxidation of the furanocyclophane VI in methanol gives a mixture of VII and a peroxidic compound, either IX or X. Sodium iodide in acetic acid reduces the peroxide to give pure VII, which is dehydrated by sodium carbonate to XI. Lithium aluminum hydride reduction, acetylation, and pyrolysis yield dihydro-*as*-indacene.

The reaction of a transition metal halide with a hydrocarbon dianion made up of two linked cyclopentadienyl anions might be anticipated to give a polymeric metallocene in which hydrocarbon rings and metal atoms alternate, a product that would be a chemical novelty. If, moreover, the cyclopentadienyl rings were joined by a planar aromatic system of unsaturated carbon atoms, the conjugation throughout the molecule would never be broken. Between each atom would be a bond that should not be effectively bicentric.[1] Consequently the electronic energy levels of the repeating units should be smeared into bands and the energy gap between the filled molecular orbital of highest energy and the unfilled orbital of lowest energy should be reduced, conferring upon the molecule exceptional conducting properties.[2,3]

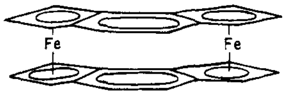
Attempts to prepare such a substance by the reaction of transition metal halides with the pentalene dianion[5] (I) have not yet been effective,[6] and alternative ligands in which two cyclopentadienyl rings are joined in a planar conjugated array have therefore been sought. The *as*-indacenyl dianion (II) was synthesized[7] and its reaction with ferrous chloride studied.[8] The reaction was found to give a ferrocene, $(C_{12}H_8Fe)_n$, which although not a high polymer, proved indeed to be a dimer. It was presumed to have either the structure III or IV, although the extent to which the central ring resembles benzene and the outer rings ferrocene required further study. Bis(*as*-indacenyliron) is the only substance known in which two metal atoms are sandwiched between a pair of planar hydrocarbon rings. Related substances are the [1,1]ferrocenophane V,[9] some polyferrocenylmethanes,[10,11] and the polyferrocenylenes,[10,12] in all of which the conjugation either is interrupted by a saturated carbon atom or may be interrupted by rotation about an inter-ring carbon–carbon single bond.[13]



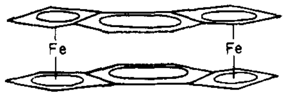
I



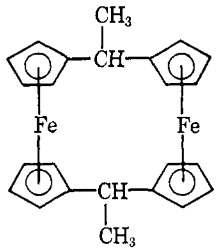
II



III



IV



V

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[1] (a) M. Rosenblum, "Chemistry of the Iron Group Metallocenes: Ferrocene, Ruthenocene, and Osmocene," Part 1, Interscience Publishers, Inc., New York, N. Y., 1965, Chapter 2; (b) D. A. Brown in "Transition Metal Chemistry," Vol. 3, R. L. Carlin, Ed., Marcel Dekker Inc., New York, N. Y., 1966, p 2 ff; (c) F. A. Cotton and G. Wilkinson, "Progress in Inorganic Chemistry," Vol. 1, F. A. Cotton, Ed., Interscience Publishers, Inc., New York, N. Y., 1959, p 86.

[2] G. Kittel, "Introduction to Solid State Physics," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1962, Chapter 11.

[3] The electronic absorption spectra of substituted ferrocenes have, however, suggested that the iron atom does not serve to conjugate the two rings [M. Rosenblum, J. O. Santer, and W. G. Howells, *J. Am. Chem. Soc.*, **85**, 1450 (1963); R. T. Lundquist and M. Cais, *J. Org. Chem.*, 27, 1167 (1962)]. This interpretation was made in the absence of a completely satisfactory theory for the bonding in ferrocene.[4]

[4] (a) A. T. Armstrong, F. Smith, E. Elder, and S. P. McGlynn, *J. Chem. Phys.*, **46**, 4321 (1967); (b) D. R. Scott and R. S. Becker, *ibid.*, **35**, 516, 2246 (1961); (c) J. C. D. Brand and W. Snedden, *Trans. Faraday Soc.*, **53**, 894 (1957).

[5] (a) T. J. Katz and M. Rosenberger, *J. Am. Chem. Soc,*, **84**, 865 (1962); (b) T. J. Katz, M. Rosenberger, and R. K. O'Hara, *ibid.*, **86**, 249 (1964).

[6] Experiments performed in this laboratory. Some simple metallocene derivatives of pentalene have, however, been prepared [T. J. Katz and M. Rosenberger, *ibid.*, **85**, 2026 (1963); T. J. Katz and J. J. Mrowca, *ibid*, **89**, 1105 (1967)].

[7] (a) The *s*-indacenyl dianion was reported by K. Hafner, *Angew. Chem. Intern. Ed. Engl.*, **3**, 165 (1964). (b) The hexacarbomethoxy-*s*-indacenyl dianion is described by E. LeGoff and R. B. LaCount, *Tetrahedron Letters*, 1161 (1964).

[8] T. J. Katz and J. Schulman, *J. Am. Chem. Soc.*, **86**, 3169 (1964).

[9] (a) W. E. Watts, *ibid.*, **88**, 855 (1966); (b) J. S. McKechnie, B. Bersted, I. C. Paul, and W. E. Watts, *J. Organometal. Chem.* (Amsterdam), **8**, P29 (1967).

[10] M. Dub, Ed., "Organometallic Compounds," Vol. 1, 2nd ed, Springer-Verlag, New York, N. Y., 1966, p 463 ff.

[11] (a) E. W. Neuse and W. G. Howells, *J. Org. Chem.*, **30**, 4071 (1965); (b) E. W. Neuse, *J. Organometal. Chem.* (Amsterdam), **6**, 92 (1966); (c) E. W. Neuse and K. Kazuko, *Bull. Chem. Soc. Japan*, **39**, 1502 (1966); (d) E. W. Neuse and E. Zuo, *ibid.*, **39**, 1508 (1966).

[12] (a) H. Rosenberg and E. W. Neuse, *J. Organometal. Chem.* (Amsterdam), **6**, 76 (1966); (b) E. W. Neuse and R. K. Crossland, *ibid.*, **7**, 344 (1967); (c) H. Watanabe, I. Motoyama, and K. Hata, *Bull. Chem. Soc. Japan*, **39**, 790 (1966); (d) I. G. Spillners and J. P. Pellegrini, *J. Org. Chem.*, **30**, 3800 (1965); (e) M. D. Rausch, *J. Am. Chem. Soc.*, **89**, 5732 (1967); (f) K. L. Rinehart, Jr., and D. G. Ries, Abstracts, 146th National Meeting of the American Chemical Society, Denver, Colo., Jan 19, 1964, p 23C.

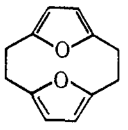
[13] (a) In crystalline biferrocenyl the rings joined by a carbon–carbon bond are coplanar [A. C. MacDonald and J. Trotter, *Acta Cryst.*, **17**, 872 (1964); Z. Kaluski, *Bull. Acad. Polon. Sci. Ser. Sci. Chim.*, **12**, 873 (1964); Z. D. Zaluski, Yu. T. Struchkov, and P. L. Avoyan, *Zh. Strukt. Khim.*, **5**, 743 (1964)]. (b) In biphenyl, a related structure, the two rings are not coplanar in the gas, but are in the

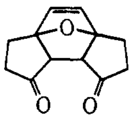
In bis(*as*-indacenyliron) the iron atoms should be sufficiently far apart so as not to interact strongly. Assuming the rings to be regular polygons with carbon–carbon bond lengths of 1.40 Å, the distance between the centers of the five-membered rings in the indacene ligand should be 3.8 Å, considerably greater than the iron–iron distance (2.4 to 2.9 Å) in compounds with bonded iron atoms.[14] In the pentalene system (I), however, the distance between ring centers should be about 1.93 Å, much smaller than the usual metal-metal bond distance, and no compound analogous to bis(*as*-indacenyliron) has been prepared with this ligand.

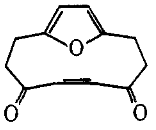
The synthesis of bis(*as*-indacenyliron) is elaborated below.

## Results

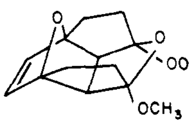
For the synthesis use was made of the discovery by Wasserman and Doumaux[15] that photooxidation of the readily preparable[16] furanocyclophane VI yields the oxy diketone VII, a reaction that appears to occur through the intramolecular Diels–Alder condensation[17] of the diene and dienophile portions of a presumed intermediate, the furan ene dione VIII. A number of changes in procedure made the reaction more efficient for use in a multistep synthesis. Among these was a change of solvent from ethanol to methanol because the scale on which the reaction can be run is limited by the solubility of the furanocyclophane, which is greater in methanol. In this solvent, with rose bengal as the photosensitizer, 1 mol of oxygen was absorbed upon irradiation, but only small amounts of the oxy diketone VII crystallized when the reaction mixture was concentrated and cooled. Significant amounts of an impurity were present.


VI

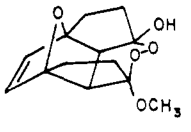

VII


VIII

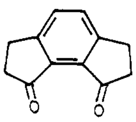
The composition of this impurity, isolated by repeated crystallization, was $C_{13}H_{16}O_5$, corresponding to the furanocyclophane VI plus $O_2$ plus $CH_3OH$. Its infrared spectrum showed that it lacked a carbonyl group, but possessed an O–H bond. Its nmr spectrum (Figure 1, bottom) is similar to that of the oxy diketone VII, except that there is an added $OCH_3$ resonance at $\tau$ 6.54 and two of the hydrogens produce an AB quartet at $\tau$ 7.11 and 7.38 ($J$ = 6.5 Hz). The probable structures for this substance are IX or X. In either case reduction with sodium iodide in acetic acid[18] should give the oxy diketone VII, verified when the crude solid reaction product of the photooxidation was treated with these reagents. Iodine was liberated and pure oxy diketone VII resulted in good yield. Since brief exposure of this compound to sodium carbonate solution results in its dehydration to 1,8-dioxo-2,3,6,7-tetrahydro-*as*-indacene (XI), the procedure used to convert the furanocyclophane VI to the aromatic ketone XI was to photooxidize a saturated solution in methanol, concentrate the solution, and add sodium iodide in acetic acid, then sodium thiosulfate to reduce the iodine, and finally sodium carbonate. The aromatic diketone XI resulted in 80% yield.



IX

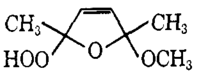


X

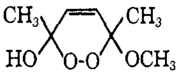

XI

When the reaction product from the photooxidation was treated with sodium carbonate without prior reduction, a mixture was produced whose nmr spectrum (*cf.* Figure 1) was that of the aromatic diketone XI with the impurity IX or X superimposed. From this mixture the ketone XI could be isolated by crystallization from methanol, but in only 40% yield.

We do not know whether the impurity has the structure IX or X. However, a similar photooxidation of 2,5-dimethylfuran gives XII, not XIII,[19] suggesting that the structure IX is correct. In agreement is the observation that the position of the nmr (Figure 1) of the hydroxyl proton, $\tau$ 0.92, is close to where the analogous resonance is found for XII[19] and other hydroperoxides,[20] while alcohols usually exhibit hydroxyl resonances at considerably higher magnetic fields.[20,21] However, a criterion previously applied to distinguish alcohols and hydroperoxides—the observation[19] that the former exhibit in dilute solution a hydroxyl infrared absorption at 2.76 ± 0.01 $\mu$ and hydroperoxides at 2.82 ± 0.01 $\mu$—failed, for the absorption was in neither of the two characteristic regions: a 0.005 $M$ solution in carbon tetrachloride exhibited an infrared peak at 2.94 $\mu$. While the structure of the peroxidic impurity is therefore not certain, it is likely to be IX, which would mean that the intramolecular Diels–Alder reaction by which it is presumably formed occurred easily although no unsaturated group was conjugated with the dienophile double bond.[22]



XII



XIII

The only stereochemistry possible for the compound is one in which the diene has added to the dienophile to give the *exo* product. Since reduction with sodium

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crystals: J. Trotter, *Acta Cryst.*, **14**, 1135 (1961); A. Hargreaves and S. H. Rizvi, *ibid.*, **15**, 365 (1962); G. B. Robertson, *Nature*, **191**, 593 (1961). (c) Conductivity measurements have been made on poly-*p*-phenylenes: F. Beck, *Ber. Bunsenges. Physik. Chem.*, **68**, 558 (1964).

(14) M. R. Churchill, *Inorg. Chem.*, **6**, 1901 (1967).

(15) H. H. Wasserman and A. R. Doumaux, Jr., *J. Am. Chem. Soc.*, **84**, 4611 (1962).

(16) H. E. Winberg, F. S. Fawcett, W. E. Mochel, and C. W. Theobald, *ibid.*, **82**, 1428 (1960).

(17) H. O. House and T. H. Cronin, *J. Org. Chem.*, **30**, 1061 (1965), and references therein.

(18) A. Nickon and J. F. Bagli, *J. Am. Chem. Soc.*, **83**, 1498 (1961).

(19) C. S. Foote, M. T. Wuesthoff, S. Wexler, I. G. Burstain, R. Denny, G. O. Schenck, and K.-H. Schulte-Elte, *Tetrahedron Letters*, 2583 (1967).

(20) (a) *t*-Butyl hydroperoxide at $\tau$ 1.08.[19] (b) S. Fujiwara, M. Katazama, and S. Kamio, *Bull. Chem. Soc. Japan*, **32**, 657 (1959).

(21) The position of the resonance of the hydroxyl protons of alcohols (and hydroperoxides[19]) is dependent on concentration and temperature. Alcohols at infinite dilution in $CCl_4$ appear near $\tau$ 9.5 (L. M. Jackman "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press Inc., New York, N. Y., 1959). At higher concentrations the resonance moves to lower field [M. Saunders and J. P. Hyne, *J. Chem. Phys.*, **29**, 1319 (1958)], but under the usual conditions of the proton nmr experiment the resonance appears between $\tau$ 6.5 and 8.5 (N. S. Bhacca, D. P. Hollis, L. F. Johnson, and E. A. Pier, "NMR Spectra Catalog," Vol. 2, Varian Associates, Palo Alto, Calif., 1963).

(22) This might be related to the observation that cyclopentadienone ketals dimerize much more readily than does cyclopentadiene [P. E. Eaton and R. A. Hudson, *J. Am. Chem. Soc.*, **87**, 2769 (1965)].

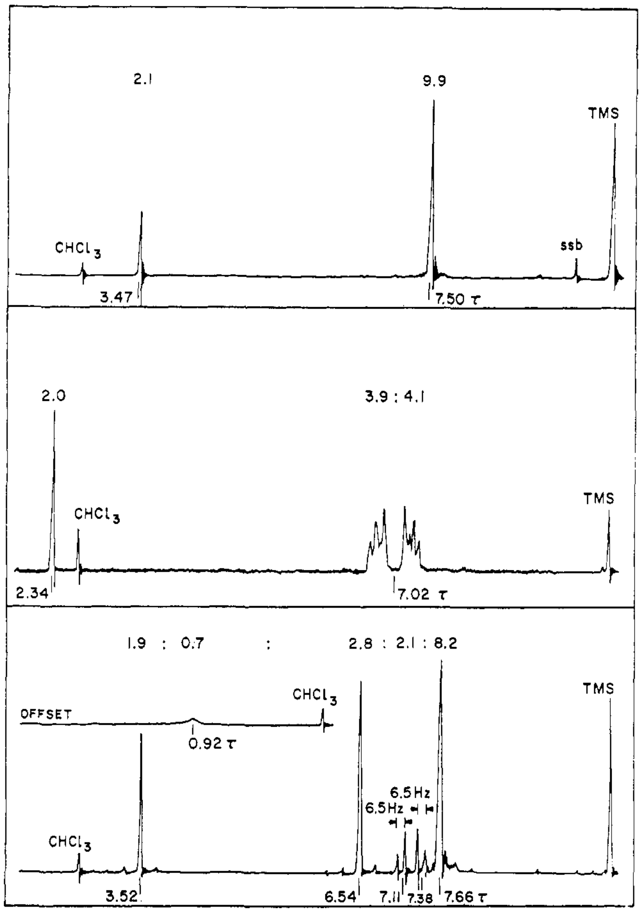
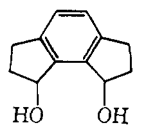


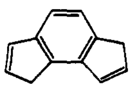
Figure 1. Nmr spectra (60 MHz) of VII (top), XI (middle), and IX or X (bottom). The solvent in each case is $CDCl_3$ and TMS is present as the internal standard. Intensities are above the peaks. The peak labeled ssb is a spinning side band.

iodide in acetic acid gives the oxy diketone VII, this substance probably also has the *exo* stereochemistry,[23] as in fact seems required by the restraints of the highly bridged structure, the dihedral angle between the bridgehead and the *exo* positions of a norbornane being smaller than the corresponding angle for the *endo* positions.

Lithium aluminum hydride reduction of the diketone XI yields the diols XIV, a mixture (approximately 2:1) of *cis* and *trans* isomers. Although this mixture was not usually separated, the individual isomers could be isolated by fractional crystallization and each acetylated with acetic anhydride in pyridine. Acetylation of the mixture of diols gave a mixture of diacetates, which when pyrolyzed at 595° gave in up to 92% yield the dihydro-*as*-indacenes XV or double bond isomers.



XIV



XV

That the hydrocarbon was dihydro-*as*-indacene was indicated by its analysis, its mass and nmr spectra, and its hydrogenation to hexahydro-*as*-indacene.[24]

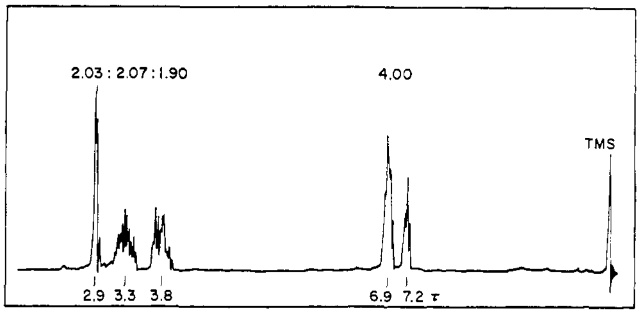


Figure 2. Nmr spectrum (60 MHz) of dihydro-*as*-indacene (neat liquid). Intensities are above the peaks. Tetramethylsilane (TMS) is the internal standard.

That the double bonds are not simply in the same positions as the hydroxyls in the diols XIV was indicated by the complexity of dihydro-*as*-indacene's nmr spectrum, particularly by the appearance of resonances attributable to two different methylene groups, at τ 6.92 and 7.20 (Figure 2).

The hydrocarbon in dimethoxyethane reacts with *n*-butyllithium to give dilithium *as*-indacenide,[25] a white crystalline precipitate that is not appreciably soluble in dimethoxyethane but is soluble in tetrahydrofuran. That dilithiation had occurred, and no other reaction such as addition of the alkyllithium to the double bonds, was shown by quenching the salt with deuterium oxide, which yielded dihydro-*as*-indacene that combustion analysis showed was dideuterated and that the peak intensities in the nmr spectrum showed was deuterated in the allylic positions. That the product was the lithium salt of the *as*-indacenyl dianion II was implied by its nmr spectrum, determined in tetrahydrofuran solution. The spectrum, displayed elsewhere[8,28] and analyzed by Schulman,[28] consists of a singlet at τ 3.16, attributable to the protons on the six-membered rings, and an ABX pattern ($\tau_A$ 4.08, $\tau_B$ 4.16, $\tau_X$ 3.94, $J_{AB}$ = ±2.1 Hz, $J_{AX} = J_{BX}$ = ±3.1 Hz), attributable to the three protons of the five-membered ring. The positions of these resonances are in agreement with those expected if one assumes that the resonances should appear where those of benzene and lithium cyclopentadienide do, taking into account appropriate corrections for (1) the perturbations owing to the ring current effects in adjacent rings[29] and (2) the effects of π-electron charge density on proton chemical shifts.[30,31] The first correction was made using the simple point-dipole approximation and the second using the assumption that proton chemical shifts vary linearly with Hückel charge densities. Details are in the Experimental Section.

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(23) This is the opposite stereochemistry from that originally suggested.[15]

(24) (a) H. Rapport and G. Smolinsky, *J. Am. Chem. Soc.*, **82**, 1171 (1960). (b) We thank Professor Harry Wasserman for a sample. *Cf.* ref 15, and its footnote 7.

(25) The reaction is similar to that used to prepare salts of the pentalene dianion,[5] the dibenzopentalene dianion,[26] the azapentalene dianion,[27] and the anions of metallocene derivatives of hydropentalene.[6]

(26) A. J. Silvestri, *Tetrahedron Letters*, 855 (1963).

(27) W. Okamura and T. J. Katz, *ibid.*, 2941 (1967).

(28) J. M. Schulman, Dissertation, Columbia University, 1964.

(29) J. W. Emsley, J. Feeney, and L. J. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Vol. 1, Pergamon Press Inc., New York, N. Y., 1965, p 141 ff.

(30) (a) G. Fraenkel, R. E. Carter, A. McLachlan, and J. H. Richards, *J. Am. Chem. Soc.*, **82**, 5846 (1960); (b) T. Schaeffer and W. G. Schneider, *Can. J. Chem.*, **41**, 966 (1963).

(31) (a) T. J. Katz, *J. Am. Chem. Soc.*, **82**, 3784 (1960); (b) T. J. Katz and P. J. Garratt, *ibid.*, **85**, 2852 (1963); **86**, 5194 (1964); (c) E. A. LaLancette and R. E. Benson, *ibid.*, **85**, 2853 (1963); **87**, 1941 (1965); (d) T. J. Katz, M. Yoshida, and L. C. Siew, *ibid.*, **87**, 4516 (1965).

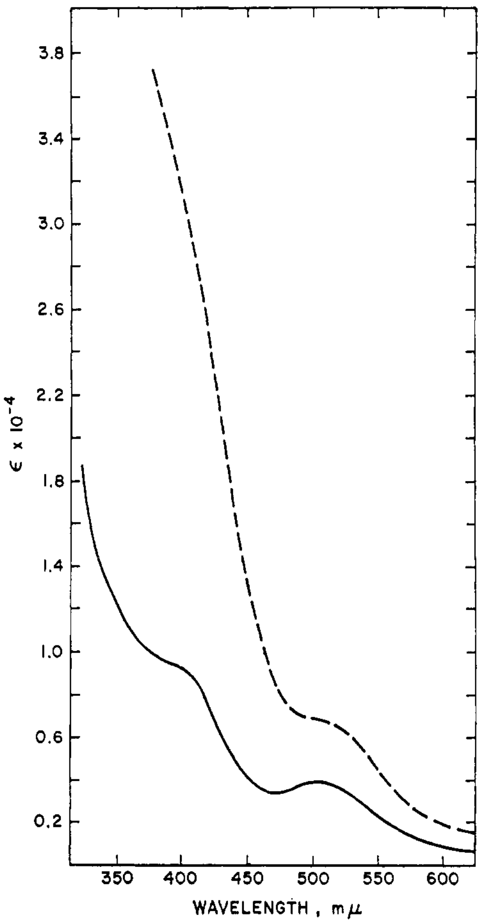

Figure 3. Ultraviolet spectrum of bis(*as*-indacenyliron): ———, in $CH_2Cl_2$; - - - -, in $CS_2$.

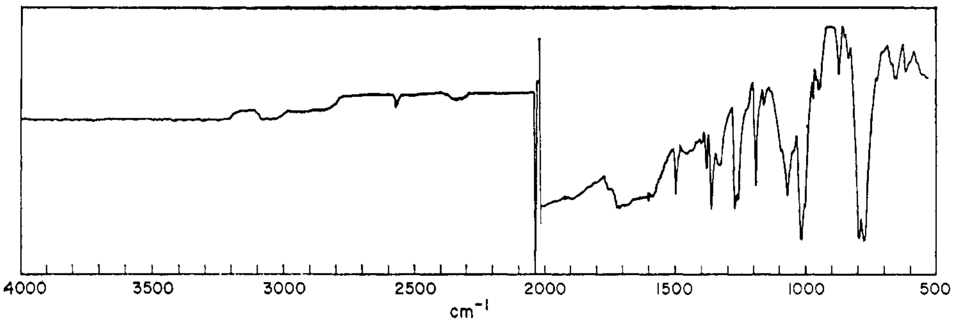

Figure 4. Infrared spectrum of bis(*as*-indacenyliron) in a KBr pellet.

Dilithium *as*-indacenide, prepared in tetrahydrofuran solution from dihydro-*as*-indacene and *n*-butyllithium, reacts with ferrous chloride to give bis(*as*-indacenyliron), presumably III or IV, in up to 87% yield. The composition of the product was shown by elemental analysis and its molecular weight by mass spectrometry.

At 75 V the mass spectrum (described in the Experimental Section), like that of other ferrocenes,[9,32] showed as the most intense peak the parent ion with the most common isotopic abundances. The intensity of the peak of one higher mass unit was that expected from the known abundances of other isotopes and the composition of the compound.[33] The mass spectrum is remarkably simple even when the ionizing voltage is 75 V. Among the few peaks observed are those corresponding to the mass of the parent ion, half that mass, and the mass of *as*-indacene. Less intense but significant peaks are at 300 and 301, corresponding to loss of both iron atoms and four or three hydrogens, and the linking of the two ring residues. These are apparently analogous to the peaks in the spectrum of ferrocene attributed to $C_5H_5C_5H_4^+$ and $C_5H_4{=}C_5H_4^+$.[32b]

The ferrocene is a maroon crystalline solid insoluble in many polar solvents and only very slightly soluble in carbon disulfide, methylene chloride, benzene, and tetrahydrofuran. The compound does not melt below 350°, and it can be slowly sublimed at 150° ($10^{-6}$ mm). The electronic spectrum, determined in methylene chloride and in carbon disulfide (Figure 3), is similar to that of ferrocene[4] but shifted to higher wavelengths. The extinction coefficients in the range of concentrations from $5.5 \times 10^{-4}$ *M* to $2.2 \times 10^{-3}$ *M* in methylene chloride and $4.8 \times 10^{-4}$ to $1 \times 10^{-3}$ *M* in carbon disulfide are independent of concentration, but dependent on the solvent; in methylene chloride $\lambda_{max}$ 504 mμ (ε 382) and 393.5 mμ (ε 940). In $CS_2$ there is a shoulder at *ca.* 500 mμ (ε 690). The compound was characterized by its infrared spectrum (Figure 4).

Slow evaporation of solvent in an argon atmosphere from a carbon disulfide solution gave large crystals suitable for X-ray analysis. X-Ray diffraction experiments showed that the space group symmetry is $P2_1/c$ and that there are two molecules of $C_{24}H_{16}Fe_2$ in the unit cell, requiring in the absence of crystal disorder that the molecules have a center of symmetry.[34] Of the structures III and IV, the latter must therefore be correct for these crystals.

## Experimental Section

**5,5-Ethylene-1,2-di-(2-furyl)ethane (Furanocyclophane, VI).**[16] 5-Methyl-2-furfuryldimethylamine was prepared at three times the scale published.[35] The reactants were combined, and heated during 2.5 hr of stirring. The yield was 84%. The resulting amine was quaternized by treating a solution of 328 g in 1.2 l. of ether with 450 g of methyl iodide. The formation of a copious precipitate prevented effective stirring, but after recrystallization from 2 l. of 1-propanol, an 87% yield of the methiodide was obtained (mp 160–161°). The iodide was converted into the hydroxide by treating 528 g in 820 ml of water with 264 g of silver oxide, washing the precipitated silver iodide, and removing the water

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[32] (a) L. Friedman, A. P. Irsa, and G. Wilkinson, *J. Am. Chem. Soc.*, **77**, 3689 (1955); (b) A. Mandelbaum and M. Cais, *Tetrahedron Letters*, 3847 (1964).

[33] K. Biemann, "Mass Spectrometry," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 59 ff.

[34] These are results of Professor Iain C. Paul (University of Illinois), who is determining the structure by X-ray diffraction.

[35] R. F. Holdren and R. M. Hixon, *J. Am. Chem. Soc.*, **68**, 1198 (1946).

either by distillation at 30° (0.1 mm) or by lyophilization. The hygroscopic product was dried to constant weight in a vacuum desiccator over $P_2O_5$. The yield was 94%.

The hydroxide (130 g) was pyrolyzed by heating it in an oil bath at 150–155° (0.2 mm). Volatile products were trapped in 100 ml of absolute ethanol containing 1.2 g of hydroquinone. The traps were washed with 120 ml of alcohol containing 0.2 g of hydroquinone, and the combined solution was refluxed for 2 hr. The furanocyclophane precipitated and was recrystallized from methylene chloride.[36] Yields were between 65 and 77%. The melting point was 190°.

**Photooxidation of VI.** As much as 20 g of VI could be photooxidized in 4 l. of methanol, but earlier experiments used only 14 g. The furanocyclophane VI (14 g, 0.074 mol) in 4 l. of methanol containing 72 mg of rose bengal dye was irradiated with a 650-W Sylvania sun-gun movie lamp (cooled by a flow of compressed air) suspended in a water-cooled jacket.[19,37] Oxygen was pumped through the solution from a gas buret by means of a circulating pump. The temperature in the reaction flask was 38 ± 2°. The required amount of oxygen (1800 ml) was consumed in about 1 hr. The solution was concentrated on a rotary evaporator to 250 ml and half was stirred with 23 g of sodium iodide in 29 ml of water and 10 ml of acetic acid.[18] After 1 hr, sodium thiosulfate was added until the iodine color disappeared. Sodium carbonate (10 g) in water (*ca.* 30 ml) was added to neutralize the acid, and then another 150 ml of saturated sodium carbonate was added in the course of 5 min to catalyze the dehydration.[38] The mixture was stirred for 30 min. Water (300 ml) was added, and the solution was extracted three times with chloroform (450 ml). Drying ($Na_2SO_4$), filtration, and evaporation of solvent gave 5.6 g (81%) of a pale yellow solid melting at 193–195°. The nmr spectrum of the material differed little from that of the recrystallized compound, mp 208–209°. The crude material was therefore used without further purification.

In other less satisfactory photooxidations water (200 ml) and zinc dust (10 g) were added to the methanol solution of the furanocyclophane and irradiated by shining two 150-W photoflood lamps on the flask. The absorption of oxygen was slow, but after completion of the reaction the oxy diketone VII and the peroxidic impurity IX or X were isolated, and after treatment with sodium carbonate, the aromatic diketone XI. The isolation of these compounds is described below.

**Isolation of Oxy Diketone VII.** After photooxidation of 14 g of VI the solution was concentrated to 300 ml and cooled to 0°, whereupon 2.6 g of VII crystallized, mp 184–186° (lit.[15] mp 186–187°). Its infrared spectrum in $CHCl_3$ has a peak at 1755 $cm^{-1}$.

**Isolation of IX or X.** In a similar experiment after the solution was concentrated to 200 ml and cooled to 0°, 7.8 g of white crystals precipitated what the nmr showed was a mixture of VII with the peroxidic impurity. After four recrystallizations from methanol 1.5 g of pure IX or X was obtained, mp 130° dec.

The infrared spectrum of the compound as a 0.005 *M* solution in $CCl_4$ was determined in 1-cm path length silica cells using a double beam Perkin-Elmer Model 421 spectrometer with expanded scale and slit width set at 120 $\mu$. The spectrum was calibrated using the absorption of the atmosphere. There was a single broad hydroxyl absorption centered about 3398 $cm^{-1}$.

*Anal.* Calcd for $C_{13}H_{16}O_5$: C, 61.89; H, 6.40. Found: C, 61.76; H, 6.22.

**Isolation of XI.** In a similar experiment, after concentration of the solvent to *ca.* 400 ml, 290 ml of saturated aqueous sodium carbonate was added in the course of 10 min while stirring, and after another 15 min, water was added and the mixture extracted with $CHCl_3$. After drying over $Na_2SO_4$ and removing the solvent, a yellow-orange solid, mp 150°, remained, whose nmr spectrum showed it to be a mixture of XI with IX or X and possibly some VII. Recrystallization from methanol furnished 5.7 g (41%) of XI, mp 208–209° (lit.[15] mp 208–209.5°). Its infrared spectrum in $CHCl_3$ has a maximum at 1728 $cm^{-1}$ and shoulders at 1745 and 1783 $cm^{-1}$.

**Reduction of IX or X to VII.** A mixture (0.4 g) of IX or X with VII, which was obtained as a photooxidation product and which melted between 100 and 130°, was dissolved in 20 ml of methanol, and a solution of 1.5 g of sodium iodide in 50 ml of water and 5 ml of acetic acid was added. After 10 min, sodium thiosulfate solution was added until the solution's color faded. Extraction with chloroform (two 70-ml portions), washing the chloroform solutions with water (three 50-ml portions), drying ($Na_2SO_4$), and removing the solvent yielded 0.36 g of VII, mp 182–184°.

**1,8-Dihydroxy-1,2,3,6,7,8-hexahydro-*as*-indacene (XIV).** Anhydrous ether (1200 ml) and $LiAlH_4$ (4.5 g, 0.12 mol) were refluxed in a 2-l., three-necked flask fitted with a stirrer and a condenser. Solid diketone XI (7.3 g, 0.039 mol) was added in small portions during a 1-hr period. After another 6-hr reflux, the reaction, while cooling in an ice bath, was quenched by adding 4.5 ml of water, then 4.5 ml of 15% NaOH, and then 13.5 ml of water.[39] The ether was filtered and the precipitate washed with 400-ml more ether. Removal of solvent left 6.2 g (84%) of a white solid, mp 92–100°, a mixture of the *cis* and *trans* diols. That the product was a mixture of diols was indicated by the presence of two singlets in the nmr spectrum at $\tau$ 2.83 and 2.87, attributable to two different aromatic protons.

Repeated recrystallization of a sample from 50:50 benzene–*n*-hexane yielded diol isomer A, mp 143.6–144.1°.[28]

*Anal.* Calcd for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42. Found: C, 75.91; H, 7.64.

Concentration of the mother liquors and recrystallization of the residue from aqueous methanol gave pure isomer B, mp 111.0–111.8°[28]

**Preparation of 1,8-Diacetoxy-1,2,3,6,7,8-hexahydro-*as*-indacenes.** A mixture of the diol isomers (6 g, 32 mmol) in a 250-ml erlenmeyer flask was dissolved in dry pyridine (47 ml). Acetic anhydride (12 ml, 120 mmol) was added, and the flask was sealed. After standing at room temperature for 20 hr, the reaction mixture was poured onto *ca.* 300 ml of ice–water, and the white precipitate was filtered and washed three times with 100-ml portions of 2% HCl and then with 450 ml of water. The precipitate was dissolved in 500 ml of ether and dried over $Na_2SO_4$. Evaporation of the solvent left 7.7 g (88%) of 1,8-diacetoxy-1,2,3,6,7,8-hexahydro-*as*-indacenes. The nmr spectrum in $CCl_4$ showed aromatic, olefinic, and other protons in the intensity ratio 2.0:2.1:13.9, as required; that this was a mixture of two diacetates (presumably the *cis* and *trans* isomers) was indicated by two singlets attributable to different aromatic protons, at $\tau$ 2.83 and 2.86, and two singlets attributable to different acetate methyls, at $\tau$ 8.03 and 8.10.

The diol isomer A (0.82 g) in a similar way gave 1.0 g (86%) of a diacetate melting at 130–132°. After two recrystallizations from benzene the melting point was 131.1–132.6°.[28]

Similarly diol B (0.26 g) gave 0.34 g (90%) of a diacetate, which after two recrystallizations from methanol melted at 148.6–150.0°.[28]

*Anal.* Calcd for $C_{16}H_{18}O_4$: C, 70.05; H, 6.61. Found: C, 69.99; H, 6.38.

**The Dihydro-*as*-indacenes (XV).** The mixture of acetates (2.5 g, 9.12 mmol) was distilled from a retort-shaped vessel into the top of a quartz tube containing quartz chips, mounted vertically in a furnace heated to 595°. A nitrogen stream flowed through a flowmeter, past a manometer, and over hot copper and a drying tube into the retort. The gas stream emerging from the bottom of the quartz tube passed through three traps cooled with Dry Ice and then to a pump. The pressure was maintained at *ca.* 10 mm. The contact time of the vapors in the furnace was 0.5 sec.

The contents of the traps were dissolved in pentane (50 ml) and extracted with saturated aqueous $NaHCO_3$ (50 ml). The bicarbonate washings were reextracted with pentane, and the combined pentane solutions were dried over $Na_2SO_4$. Filtration and evaporation of solvent left a yellow mixture of liquid and crystals that solidified at *ca.* 10°. The yield was 1.35 g (92%).

The hydrocarbon was recrystallized three times from *n*-pentane at −78° and sublimed ($10^{-6}$ mm). It was crystalline at 20°, but partially liquid at 27°.

*Anal.* Calcd for $C_{12}H_{10}$: C, 93.46; H, 6.54. Found: C, 93.67; H, 6.71.

Its ultraviolet spectrum in cyclohexane is complex, with maxima or shoulders at ($\lambda$ m$\mu$ (log $\epsilon$)) 234 (4.57), 241 (3.98), 252 (4.40), 267 (4.38), 278 (4.28), 283–289 (3.98), 301 (3.83), and 305 (3.72).

**Hydrogenation of Dihydro-*as*-indacene.** The mixture of dihydro-*as*-indacene isomers (250 mg, 1.62 mol) was hydrogenated at 27° at atmospheric pressure in absolute ethanol using 5% Pd–C catalyst. Filtration and removal of solvent left an oil, which was

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[36] Soxhlet extraction[16] was not necessary.

[37] G. O. Schenck, *Angew. Chem.*, **68**, 12 (1952).

[38] Dilute sulfuric acid, which is reported to effect the dehydration,[15] failed to do so when we tried it. Sodium carbonate, however, was effective.

[39] V. M. Mićović and M. L. J. Mihailović, *J. Org. Chem.*, **18**, 1190 (1953).

eluted through a silica gel column with petroleum ether. Hexahydro-*as*-indacene (239 mg, 96%), a colorless oil present in the first fractions, crystallized on cooling and was sublimed (0.1 mm). It melted at 39.0–40.8° and did not depress the melting point of an authentic sample, mp 40.5–41.0°, and its infrared, ultraviolet, and nmr spectra were superimposable on those of the authentic material.[24]

**Dilithium *as*-Indacenide (II).** Lithium *as*-indacenide was prepared in a nitrogen atmosphere in flame-dried glass apparatus. Dihydro-*as*-indacene (150 mg, 0.97 mmol) in dry dimethoxyethane (3.0 ml) was cooled to −78°, and *n*-butyllithium (2.0 ml, 2.3 mmol) in *n*-hexane was slowly added through a serum bottle cap by means of a hypodermic syringe. A yellow color and a thick orange precipitate appeared. The mixture was stirred and warmed to room temperature. At −20° the precipitated salt became white and the supernatant liquid amber. The mixture was stirred for 40 min at room temperature.

**Nmr Spectrum of Dilithium *as*-Indacenide.** To determine the nmr spectrum the precipitate was filtered under nitrogen onto a sintered disk fused to the reaction vessel and was washed twice with 2-ml aliquots of dimethoxyethane. The precipitate was then dissolved in dry tetrahydrofuran, and the solution was tipped into an nmr sample tube also fused to the apparatus. The apparatus was evacuated, and the tube was fused and drawn free. The nmr spectrum was determined at 100 MHz using a field sweeping Varian HR-100 spectrometer. Frequencies were measured by generating side bands of the lower field resonance of dimethoxyethane. The spectrum was also determined at 60 MHz using a Varian A-60 spectrometer. The chemical shifts were placed on the $\tau$ scale by assuming that the low-field dimethoxyethane resonance is at $\tau$ 6.46. The 100-MHz spectrum consisted of a singlet at $\tau$ 3.16 and a complex absorption, 3.2 times as intense, analyzed as an ABX pattern with $\tau_A$ 4.08, $\tau_B$ 4.16, $J_{AB} \pm 2.1$ Hz, and $J_{AX} = J_{BX} = \pm 3.1$ Hz. The 60-MHz spectrum was analyzed using similar parameters.[28] Whether the positions of the resonances were in accord with expectation was tested by a procedure similar to that used by Schaeffer and Schneider in their examination of other hydrocarbon anions.[30b] The analysis is presented in Table I using their notation. The charge density associated with carbon atoms 4 and 5 is given as $\rho = -a/10.7$, where $a$ is the corrected chemical shift minus 2.73, the chemical shift ($\tau$) of benzene. For carbons 1, 2, 3, 6, 7, and 8 the density is given as $-(0.2 + a/10.7)$, where $a$ is the corrected chemical shift minus 4.47, the chemical shift ($\tau$) of lithium cyclopentadienide in tetrahydrofuran. The average charge density at carbons 9, 10, 11, and 12 is given in the table as

$$-{}^1/_4\left(2 + \sum_{i=1}^{8} \rho_i\right)$$

Table I. Proton Chemical Shifts, Derived Electron Densities ($\rho$), and Calculated Electron Densities for Dilithium *as*-Indacenide[a]

| Proton position | Chemical shift, $\tau$ | $\delta$, ppm, ring current corrn | Chem shift cor, $\tau$ | $\rho_{\text{exptl}}$[b] | $\rho_{\text{calcd}}$ HMO |
|---|---|---|---|---|---|
| 1, 8 | 4.08 | 0.78 | 4.85 | −0.24 | −0.25 |
| 2, 7 | 3.94 | 0.35 | 4.29 | −0.18 | −0.15 |
| 3, 6 | 4.16 | 0.60 | 4.76 | −0.23 | −0.24 |
| 4, 5 | 3.16 | 0.66 | 3.82 | −0.10 | −0.08 |
| (Av 9, 10, 11, 12) | | | | −0.13 | −0.14 |

[a] The notation and procedure are based on those of T. Schaeffer and W. G. Schneider, *Can. J. Chem.*, **41**, 966 (1963). [b] The procedure used is slightly different from that of Schaeffer and Schneider. See the text.

**Reaction of Lithium *as*-Indacenide with Deuterium Oxide.** The lithium *as*-indacenide was prepared as described above. Deuterium oxide (30 ml) was injected into a vessel attached to the one in which the salt had been prepared, and with stirring, the salt suspension was then slowly poured into the water. The organic layer was extracted with pentane (50 ml), dried over $Na_2SO_4$, concentrated, and sublimed ($10^{-6}$ mm) to give deuterated dihydro-*as*-indacene.

*Anal.* Calcd for $C_{12}H_8D_2$: 20.0% excess D. Found: 19.35.

The nmr spectrum showed aromatic, olefinic, and allylic protons in the intensity ratio 2.1:3.8:2.1, implying that two deuterium atoms occupy the allylic positions of dihydro-*as*-indacene.

**Bis(*as*-indacenyliron).** The apparatus consisted of two connecting reaction vessels with standard taper joints sealed by stopcocks. The openings of the stopcocks were covered with serum bottle caps. There was a magnetic stirring bar in each vessel. The apparatus was flame dried, and the reaction was performed in an argon atmosphere. Anhydrous ferrous chloride (1.1 g, 8.59 mmol) was placed in one vessel and washed by injecting and withdrawing dry tetrahydrofuran (THF) through one stopcock. Some THF (*ca.* 3 ml) was left with the $FeCl_2$. In the other vessel, dilithium *as*-indacenide was prepared as follows. Dihydro-*as*-indacene (0.96 g, 6.24 mmol) in THF (5 ml) was cooled to −78°, and 7 ml (11.2 mmol) of 1.6 *M* *n*-butyllithium in *n*-hexane was added in drops during 5 min. During the addition the solution first turned red and later orange. After addition of the *n*-butyllithium was complete, the dilithium *as*-indacenide precipitated as white crystals, and the supernatant liquid was a dirty yellow-brown. More THF (5 ml) was added, and the mixture was allowed to come to room temperature during 15 min. More THF (2 ml) was added to dissolve the remaining solid. After another 10 min the solution was poured at room temperature into the $FeCl_2$ slurry. The solution instantly turned red. After 30 min of stirring there was a red precipitate and a blood red supernatant liquid. The mixture was filtered in an argon atmosphere and the red precipitate was washed with three 25-ml portions of dry pentane. The precipitate was extracted with a large quantity (> 1 l.) of benzene, and the solvent was removed yielding 0.89 g of a rust colored solid. From the THF and pentane filtrate another 0.16 g of material was recovered, which in this experiment was somewhat sticky but in other experiments was not. This material was isolated by removing the THF and pentane, dissolving the residue in benzene, filtering, and removing the solvent. The combined yield of bis(*as*-indacenyliron) was 1.05 g (83%). Material that had dissolved in the THF–pentane but was insoluble in benzene amounted to about 0.8 g. For analysis bis(*as*-indacenyliron) was recrystallized from benzene.

*Anal.* Calcd for $C_{24}H_{16}Fe_2$: C, 69.28; H, 3.88; Fe, 26.84. Found: C, 69.24, 69.28; H, 4.07, 3.96; Fe, 26.74, 26.95.

Bis(*as*-indacenyliron) is insoluble in $CH_3OH$, $C_2H_5OH$, $CH_3CN$, and $(C_2H_5)_2O$. It is very slightly soluble (<0.1 mg/ml) in $(CH_3)_2SO$ and in $(CH_3)_2NCHO$. It is slightly soluble (*ca.* 0.7–2.0 mg/ml) in $CS_2$, $CH_2Cl_2$, $C_6H_6$, and THF. Solutions of the ferrocene in air (rapidly in THF and slowly in $C_6H_6$) deposit a brown insoluble precipitate. Large crystals were obtained by slowly evaporating the solvent in an argon atmosphere from a solution of 5 mg of the ferrocene in 5 ml of $CS_2$.

The electronic spectrum was determined in $CH_2Cl_2$ and in $CS_2$ and is described in the text.

The mass spectrum, determined by placing the sample directly into the heated (150°) ion source of a Hitachi Model RMU-6D mass spectrometer, was remarkably simple even when the ionizing voltage was 75 V. The only peaks observed, some of which might even be spurious, were the following. Intensities as per cent of the base peak are given after *m/e:* 81 (2), 112 (4), 126 (4), 150 (5), 151 (9.0), 152 (49.0), 153 (8), 181 (2), 206 (1), 207 (5), 208 (39.0), 209 (10.0), 210 (3), 299 (2), 300 (11.0), 301 (9.0), 302 (5), 303 (3), 414 (14.0), 415 (8.5), 416 (100), 417 (32.0), and 418 (6.0). *m/e* 416 corresponds to ${}^{12}C_{24}{}^{1}H_{16}{}^{56}Fe_2{}^+$ and 417 to an ion with the same composition but different isotopes. The ratio of the intensities of the peaks at 417 and 416 should, if they have this composition and the isotopes are distributed normally, be[33] $24(1.1119) + 16(0.015) + 2(91.66)(2.19)(100)/[(91.66)^2 + 2(5.82)(0.33)] = 31.9\%$. The peak at 208 is presumably either $C_{12}H_8Fe^+$ or $C_{24}H_{16}Fe^{2+}$, and that at 152, $C_{12}H_8{}^+$.

Bis(*as*-indacenyliron) sublimes slowly at 150° ($10^{-6}$ mm).

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