# Polycyclic Systems. Part 17.[1] Proton Nuclear Magnetic Resonance Spectra of Some 11*H*-Indeno[2,1-*a*]phenanthrene Derivatives; Structure of the $C_{26}$ Hydrocarbon (Second Diels Hydrocarbon) from Cholesterol

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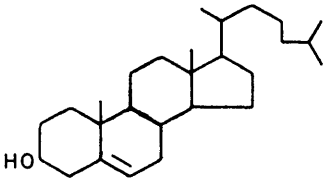
The n.m.r. spectra of a number of 11*H*-indeno[2,1-*a*]phenanthrenes, including the $C_{26}$ hydrocarbon (second Diels hydrocarbon) from cholesterol, and their 11-oxo-derivatives have been studied. These data together with some previous observations identify the hydrocarbon as 8-isobutyl-10-methyl-11*H*-indeno[2,1-*a*]phenanthrene (21), its formation being rationalised in terms of 1,2-shift of the side chain in ring D, followed by a similar shift of the 13-methyl group and its final inclusion in ring E of the indenophenanthrene (21).

ALTHOUGH most structural problems in the steroid series have long been satisfactorily solved, there still remains an ambiguity about the identity of a $C_{26}$ hydrocarbon (commonly known as the second Diels hydrocarbon) and two of its higher homologues ($C_{27}$ and $C_{28}$) obtained as minor products during dehydrogenation of cholesterol (1),[2] ergosterol,[3] and phytosterols,[4] respectively with selenium or palladium. The early formulation of the cholesterol hydrocarbon as 10-isopropyl-7-methyl-

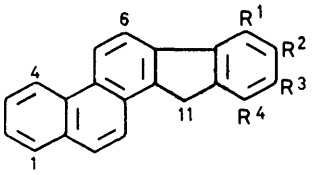
[1] Part 16, D. Nasipuri and I. De Dalal, *J.C.S. Perkin I*, 1976, 2052.
[2] O. Diels, W. Gadke, and P. Kording, *Annalen*, 1927, **459**, 1.
[3] O. Diels and A. Karstens, *Annalen*, 1930, **478**, 129; L. Ruzicka, M. W. Goldberg, and G. Thomann, *Helv. Chim. Acta*, 1933, **16**, 812; O. Diels and H. J. Stephan, *Annalen*, 1937, **527**, 279.
[4] L. Ruzicka and M. W. Goldberg, *Helv. Chim. Acta*, 1937, **20**, 1245.

11*H*-indeno[2,1-*a*]phenanthrene (7),[5] thought to arise by ring closure between the side chain and ring D [*cf.* formation of 7-methylindenophenanthrene (3) from cholic acid [6]] was effectively ruled out by a synthesis of compound (7).[7] There were, however, points of similarity suggestive of a common skeletal structure of type (2).[7] Subsequently, Bergmann formulated the compound as a $C_{26}$ hydrocarbon of structure (8), its origin being rationalised in terms of cleavage of ring D between C-13 and C-17, followed by aromatisation and double cyclisation found to be different from those derived from cholesterol and ergosterol, respectively. A revision of structure is, therefore, necessary. We now show from the the n.m.r. spectra of a number of indeno[2,1-*a*]phenanthrenes including that one from cholesterol that the $C_{26}$ hydrocarbon has the structure (21).

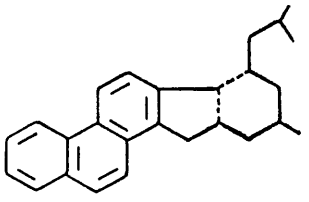
The mass spectrum of the cholesterol hydrocarbon confirmed its molecular formula as $C_{26}H_{24}$. The possibility that it might be a derivative of the isomeric 7*H*-indeno[1,2-*a*]phenanthrene (11) having the structure (12)



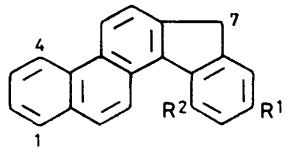

(1).



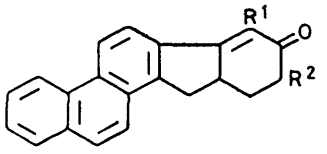

(2) $R^1 = R^2 = R^3 = R^4 = H$
(3) $R^1 = Me, R^2 = R^3 = R^4 = H$
(4) $R^1 = R^2 = R^4 = H, R^3 = Me$
(5) $R^1 = R^2 = R^3 = H, R^4 = Me$
(6) $R^1 = R^2 = Me, R^3 = R^4 = H$
(7) $R^1 = Me, R^2 = R^3 = H, R^4 = CHMe_2$
(8) $R^1 = CH_2{\cdot}CHMe_2, R^2 = R^4 = H\ R^3 = Me$
(9) $R^1 = CHMe{\cdot}CHMe_2, R^2 = R^4 = H, R^3 = Me$



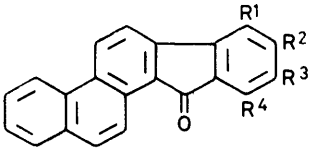
(10)



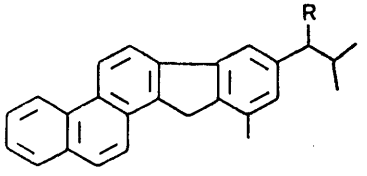

(11) $R^1 = R^2 = H$
(12) $R^1 = Me, R^2 = CH_2{\cdot}CHMe_2$




(13) $R^1 = Me, R^2 = H$
(14) $R^1 = CH_2{\cdot}CHMe_2, R^2 = Me$
(15) $R^1 = CHMe{\cdot}CHMe_2, R^2 = Me$




(16) $R^1 = Me, R^2 = R^3 = R^4 = H$
(17) $R^1 = R^2 = R^3 = H, R^4 = Me$
(18) $R^1 = R^2 = Me, R^3 = R^4 = H$
(19) $R^1 = CH_2{\cdot}CHMe_2, R^2 = R^4 = H, R^3 = Me$
(20) $R^1 = R^3 = H, R^2 = CH_2{\cdot}CHMe_2, R^4 = Me$




(21) R = H
(22) R = Me
(23) R = $CH_2Me$

of the intermediate (10) (see dotted lines).[8] The mechanism, based on the analogy of the conversion of strophanthidin, a steroidal lactone, into 9-methylindeno[2,1-*a*]-phenanthrene (4), the identity of which was never satisfactorily established, is rather unusual and unprecedented in sterols.[9] Furthermore, the two hydrocarbons (8) and (9) have been synthesised in our laboratory [10,11] and were (a result of cleavage between C-13 and C-17, reorganisation of the acyclic chain to form a substituted benzene ring, and participation of the 13-methyl group in building up a new five-membered ring [12]) was next eliminated by

[5] O. Rosenheim and H. King, *Chem. and Ind.*, 1933, **52**, 299.
[6] L. Ruzicka, G. Thomann, E. Brandenberger, M. Furter, and M. W. Goldberg, *Helv. Chim. Acta*, 1934, **17**, 200; W. E. Bachmann, J. W. Cook, C. L. Hewett, and J. Iball, *J. Chem. Soc.*, 1936, 54.
[7] J. W. Cook, C. L. Hewett, W. V. Mayneord, and E. Roe, *J. Chem. Soc.*, 1934, 1727.
[8] E. Bergmann, *J. Amer. Chem. Soc.*, 1938, **60**, 2306; see also L. F. Fieser and M. Fieser, 'Natural Products Related to Phenanthrene,' Reinhold, New York, 1949, p. 155.
[9] Z. Valenta, 'Elucidation of Organic Structures by Physical and Chemical Methods,' Part II, eds. K. W. Bentley and G. W. Kirby, Wiley–Interscience, New York, 1973, p. 47.
[10] D. Nasipuri, *J. Chem. Soc.*, 1961, 4230.
[11] D. Nasipuri, D. N. Roy, and R. C. Banerjee, *J. Indian Chem. Soc.*, 1963, **40**, 225.
[12] J. W. Cook, C. L. Hewett, W. V. Mayneord, and E. Roe, *Chem. and Ind.*, 1934, 569.

synthesis of the parent hydrocarbon (11) [13] and a study of its u.v. absorption spectrum, which was completely different from those of any of the indeno[2,1-*a*]phenanthrenes (see Experimental section). On the other hand, the u.v. spectrum of the second Diels hydrocarbon was almost identical with that of the synthetic compound (8),[11] emphasising once again a common ring system. To remove any element of uncertainty in the structure of the synthetic $C_{26}$ and $C_{27}$ hydrocarbons (8) and (9), the n.m.r spectra of the ketones (14) and (15), their immediate precursors, were checked for any possible rearrangement before or during cyclisation of the intermediate 1,5-diones.[14] The methyl signal in the spectra of both ketones appeared as a doublet (*J* 7 Hz) centred at τ 8.70, whereas that in the ketone (13) appeared at τ 7.76 (*J* 2 Hz, allylic coupling). This rules out any structure in which the positions of the methyl and the other substituent ($CH_2$·$CHMe_2$ or CHMe·$CHMe_2$) are reversed, a possibility not to be wholly ignored in syntheses with Mannich bases (*cf.* ref. 15). The n.m.r. spectra of a number of indeno[2,1-*a*]phenanthrenes and of the natural $C_{26}$ hydrocarbon (see Table) were then analysed. The natural hydrocarbon, like the synthetic one (8), showed peaks for aromatic methyl and isobutyl groups and both exhibited two aromatic proton singlets (with line broadening due to *meta*-coupling) at comparatively high field (see Figures 1 and 2 for the aromatic regions of the spectra). Clearly, these two protons belong to ring E and are non-vicinal. This leaves the two substituents, methyl and isobutyl, *meta* to each other as indeed they are in the synthetic hydrocarbon (8) and expected to be in the natural one in which the relative position of the two groups is dictated by the iso-octyl side chain. The difference in the two hydrocarbons thus lies in the positions

$^1$H N.m.r. spectra of indeno[2,1-*a*]phenanthrene derivatives (τ values) [a]

| Compound [b] | Aromatic protons | Other protons |
|---|---|---|
| (5) | 1.30 (d, *J* 9 Hz, 4- + 5-H), 1.95 (d, *J* 7 Hz, 6-H), 2.00—2.27 (m, 1- + 12- + 13-H), 2.30—2.50 (m, 2- + 3-H), 2.63 (d, *J* 9 Hz, 7-H), 2.85 (m, 8- + 9-H) | 5.91 (s, 11-$H_2$), 7.51 (s, 10-Me) |
| (6) | 1.29 (d, *J* 9 Hz, 4- + 5-H), 1.71 (d, *J* 9 Hz, 6-H), 2.03—2.30 (m, 1- + 12- + 13-H), 2.30—2.54 (m, 2- + 3-H), 2.61 (d, *J* 6 Hz, 10-H), 2.86 (d, *J* 8 Hz, 9-H) 2.30—2.54 (m, 2- + 3-H), 2.61 (d, *J* 6 Hz, 10-H), 2.86 (d, *J* 8 Hz, 9-H) | 5.82 (s, 11-$H_2$), 7.25 (s, 7-Me), 7.57 (s, 8-Me) |
| (8) | 1.32 (d, *J* 9 Hz, 4- + 5-H), 1.93 (d, *J* 9 Hz, 6-H), 2.08—2.24 (m, 1- + 12- + 13-H), 2.26—2.54 (m, 2- + 3-H), 2.73 (s, 10-H), 3.06 (s, 8-H) | 5.88 (s, 11-$H_2$), 7.04 (d, *J* 8 Hz, 7-$CH_2$), 7.58 (s, 9-Me), 7.90 (m, C*H*$Me_2$), 8.93 (d, *J* 6 Hz, $CMe_2$) |
| (21) [c] | 1.29 (d, *J* 9 Hz, 4- + 5-H), 1.98 (d, *J* 9 Hz, 6-H), 2.17—2.46 (m, 5 × ArH), 2.49 (s, 7-H), 3.05 (s, 9-H) | 5.94 (s, 11-$H_2$), 7.42 (d, *J* 8 Hz, 8-$CH_2$), 7.53 (s, 10-Me), 8.03 (m, C*H*$Me_2$), 9.01 (d, *J* 8 Hz, $CMe_2$) |
| (17) | 1.06 (d, *J* 9 Hz, 12-H), 1.33 (d, *J* 8 Hz, 4-H), 1.54br (d, *J* 6 Hz, 5-H), 2.10—2.60 (m, 6 × ArH), 2.70 (d, *J* 8 Hz, 9-H), 3.00 (m, 8-H) | 7.38 (s, 10-Me) |
| (18) | 1.04 (d, *J* 9 Hz, 12-H), 1.30 (d, *J* 8 Hz, 4-H), 1.56br (d, *J* 6 Hz, 5-H), 2.00—2.60 (m, 5 × ArH), 2.72 (d, *J* 7 Hz, 10-H), 2.95 (d, *J* 7 Hz, 9-H) | 7.43 (s, 7-Me), 7.67 (s, 8-Me) |
| (19) | 1.03 (d, *J* 8 Hz, 12-H), 1.35 (d, *J* 9 Hz, 4-H), 1.58br (d, *J* 6 Hz, 5-H), 2.10—2.57 (m, 5 × ArH), 2.73 (s, 10-H), 3.10 (s, 8-H) | 7.29 (d, *J* 7 Hz, 7-$CH_2$), 7.70 (s, 9-Me), 7.90 (m, C*H*$Me_2$), 8.95 (d, *J* 6 Hz, $CMe_2$) |
| (20) [d] | 1.00 (d, *J* 9 Hz, 12-H), 1.27 (d, *J* 8 Hz, 4-H), 1.50br (d, *J* 9 Hz, 5-H), 2.06—2.46 (m, 5 × ArH), 2.86 (s, 7-H), 3.22 (s, 9-H) | 7.39 (s, 10-Me), 7.54 (d, *J* 7 Hz, 8-$CH_2$), 8.05 (m, C*H*$Me_2$), 9.02 (d, *J* 7 Hz, $CMe_2$) |

[a] Spectra taken for solutions in $CDCl_3$ at 100 MHz. [b] Data for the rest of the compounds mentioned in this paper [compounds (2), (3), (9), and (13—16)] are available as Supplementary Publication No. SUP 22068 (6 pp.); for details see Notice to Authors No. 7, *J.C.S. Perkin I*, 1976, Index issue. [c] Second Diels hydrocarbon. [d] Ketone derived from second Diels hydrocarbon.

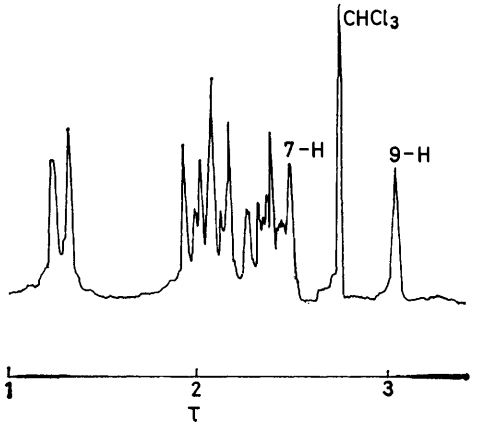



FIGURE 1

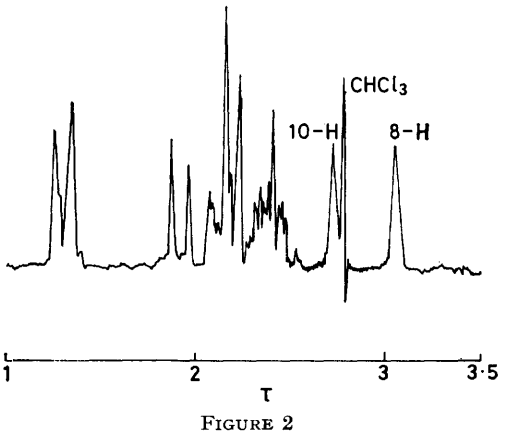



FIGURE 2

[13] N. P. Buu-Hoi and P. Cagniant, *Rev. Sci.*, 1942, **80**, 319 (*Chem. Abs.*, 1945, **39**, 3276).
[14] D. Nasipuri and D. N. Roy, *J. Chem. Soc.*, 1961, 3361.
[15] G. L. Buchanan and A. C. W. Curran, *Chem. Comm.*, 1966, 773.

of the two groups in ring E, which explains the close similarity of their mass spectra.

The next piece of evidence comes from the chemical shifts of the ring E aromatic methyl protons. The data in the Table show that 8-, 9-, and 10-methyl groups have approximately the same chemical shift (τ 7.57, 7.58, and 7.51, respectively) whereas the 7-methyl signal appears at considerably lower field [τ 7.25 in (6) and 7.17 in (3)], being deshielded by the neighbouring aromatic ring. Since the aromatic methyl group in the natural $C_{26}$ hydrocarbon resonates at τ 7.53 (a value very close to that for the 10-methyl), it cannot be at C-7. Similarly, the side chain methylene protons (7-$CH_2$) in the synthetic hydrocarbon (8) resonate at a considerably lower field (τ 7.04) than those in the natural one (7.42), indicating that the isobutyl group in the latter is also not at C-7. These facts, together with the previous observation that the methyl and isobutyl groups are *meta* to each other, suggest that the Diels hydrocarbon is best represented by structure (21) or the alternative with the positions of the two substituents reversed.

To settle this point, the n.m.r. spectra of the corresponding 11-oxo-derivatives (16)—(20) were examined. The 10-methyl signal in compound (17) is shifted downfield by 0.13 p.p.m. in comparison with compound (5), which is attributable to the diamagnetic anisotropy of the neighbouring carbonyl group.[16] A similar shift (0.14 p.p.m.) occurs for the methyl group in the 11-oxo-derivative of the second Diels hydrocarbon. The positions of the peaks are also identical in the two sets of spectra, leading to the conclusion that the methyl group in the natural ketone is at C-10 and the isobutyl group by inference at C-8, as in structure (20).

In contrast, methyl groups elsewhere in ring E, in the ketones (16), (18), and (19), and also some of the aromatic protons, resonate at slightly higher field than in their hydrocarbon counterparts. This is contrary to normal substituent shielding values,[17] and may be due to the presence of a five-membered ring with all the five carbon atoms $sp^2$-hybridised, giving rise to considerable internal strain; this could only be relieved by distortion of the molecules with partial loss of planarity and aromaticity of rings C and E. The result is a general upfield shift of the signals due to the aromatic protons and other substituents attached to these rings. This would also explain why the 10-methyl group in the ketones (17) and (20) is not deshielded to the extent (*ca.* 0.30 p.p.m.) observed in analogous systems (see for example refs. 18 and 19 for deshielding of an 8-methyl group in 1-tetralone derivatives).

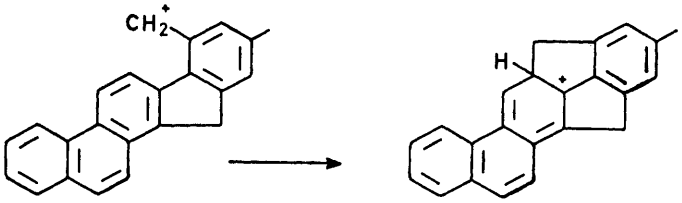
The above evidences clearly determines the structure (21) for the $C_{26}$ hydrocarbon from cholesterol, and by analogy structures (22) and (23) for those derived from ergosterol and phytosterols, respectively.

The formation of the second Diels hydrocarbon (21) from cholesterol may be envisaged as occurring through a series of 1,2-shifts initiated by an appropriate radical centre, the crucial steps being the shift of the iso-octyl side chain from C-17 to C-16 with concomitant migration of the 13-methyl group to the vacated position (a well documented process [20]) and its subsequent interaction with C-23 to build up ring E of the indenophenanthrene. The mechanism does not require the cleavage and reformation of the five-membered ring, which was the main objection to the Bergmann hypothesis.[9] Further, the probable molecular length of the cholesterol hydrocarbon calculated from the dimensions of the unit cell by *X*-ray crystallography is appreciably greater than that of 10-isopropyl-7-methyl-11*H*-indeno[2,1-*a*]phenanthrene (7),[21] and may well fit the more extended formula (21).

The structure of the second Diels hydrocarbon thus being settled, a few minor spectral details may be discussed. (i) The position of the 11-methylene signal (τ 5.94) of the cholesterol hydrocarbon is identical with that in 10-methylindenophenanthrene (5) but slightly upfield as compared with that (5.88) in its synthetic analogue (8), probably owing to the electron-donating effect [17,22] of the neighbouring 10-methyl group. (ii) In the 11-oxo-indenophenanthrenes, the highest upfield shift occurs with the 7-methyl protons (+0.25 p.p.m.), only moderate shifts being observed with 8-methyl, 9-methyl, and 8-methylene protons (+0.12 p.p.m.). Similar upfield shifts are also observed for 7-H, 6-H, and 5-H, probably in that order (*ca.* 0.37, 0.25, and 0.20 p.p.m., respectively.) This is in general agreement with the concept of the nonplanarity of rings C and E in the ketones. (iii) The 10-proton resonates at 2.73 in the hydrocarbon (8) as well in the derived ketone (19); this may be due to the nonplanarity of the molecule, the proton being neither shielded nor deshielded by the carbonyl group. Alternatively, the deshielding effect of the carbonyl might be counterbalanced by the partial loss of aromaticity. In the 7,8-dimethyl ketone (18) also the 10-proton signal appears at a similar position (2.72). The assignments of the peaks for 8-H, 9-H, and 10-H are based on the data for benzo[*a*]fluorene [23] and seem logical. The observations (ii) and (iii) tally with those for fluorene [24] and fluorenone.[25] (iv) The mass spectra of the synthetic and natural $C_{26}$ hydrocarbons differ in one important aspect; namely, the intensity of

[16] L. M. Jackman and S. Sternhell, 'Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry,' 2nd edn., Pergamon, Oxford, 1969, p. 91.
[17] K. D. Bartle and D. W. Jones, 'Advances in Organic Chemistry; Methods and Results,' vol. 8, ed. E. C. Taylor, Wiley–Interscience, New York, 1972, p. 322.
[18] R. M. Carman and W. J. Craig, *Austral. J. Chem.*, 1971, **24**, 1919.
[19] D. Nasipuri, I. De Dalal, and D. N. Roy, *J.C.S. Perkin I*, 1973, 1754.
[20] A. Cohen, J. W. Cook, and C. L. Hewett, *J. Chem. Soc.*, 1935, 446; see also E. Bergmann, *Chem. and Ind.*, 1935, **54**, 175; M. S. Bharucha, E. Weiss, and T. Reichstein, 1962, **45**, 103.
[21] J. D. Bernal and D. Crowfoot, *J. Chem. Soc.*, 1935, 93.
[22] J. W. Emsley, J. Feeney, and L. H. Sutcliffe, ' High Resolution Nuclear Magnetic Resonance Spectroscopy,' vol. 2, Pergamon, Oxford, 1963, Appendix B, p. 1115.
[23] K. D. Bartle and D. W. Jones, *Spectrochim. Acta*, 1972, **28***A*, 2053.
[24] K. D. Bartle and D. W. Jones, *J. Chem. Soc.* (*B*), 1971, 388.
[25] H. A. Szymanski and R. E. Yelin, ' N.m.r. Band Handbook,' Plenum Press, New York, 1968, p. 346.

the peak at *m/e* 293 is less than half that of the $M^+$ peak in the latter but the corresponding peaks are almost of equal intensity in the former case. This may be due to stabilisation of the ion (24) *via* the cyclised structure (25) in the synthetic compound.




## EXPERIMENTAL

$^1$H N.m.r. spectra were taken mostly with a Varian XL-100 100 MHz instrument (some with T-60, HR-100, or 270 MHz spectrophotometers), with tetramethylsilane as internal standard. Petroleum refers to the fraction of b.p. 60—80 °C.

10-*Methyl*-11H-*indeno*[2,1-a]*phenanthrene* (5).—Compound (5) was prepared essentially by the method of Bachmann *et al.*[26] with the following modifications.

2-Methyl-3-*o*-tolylpropionic acid (12.5 g) was heated with polyphosphoric acid (200 g) at 100 °C with stirring for 1½ h. The usual work-up afforded 2,4-dimethylindan-1-one as an oil (9.5 g), b.p. 140° at 10 mmHg (Found: C, 82.4; H, 7.7. Calc. for $C_{11}H_{12}O$: C, 82.5; H, 7.5%). The indanone (7.0 g) was treated with the Grignard reagent prepared from β-1-naphthylethyl bromide (15.0 g) in ether and the resultant hydrocarbon (12.5 g), b.p. 140—145° at 0.5 mmHg, was cyclised with polyphosphoric acid (350 g) by heating first at 100 °C for 2 h and finally at 150 °C for 1 h. Work-up in the usual way afforded a gum (11.5 g), b.p. 135—137° at 0.5 mmHg. This crude hydrocarbon was dehydrogenated with selenium [26] to furnish 10-methyl-11*H*-indeno[2,1-*a*]phenanthrene (5), m.p. 274—275° (from benzene–petroleum); the 11-oxo-derivative (17) had m.p. 237° (lit.,[26] 272.5—273 and 237—238°, respectively). The i.r. spectrum (KBr) of the latter showed a carbonyl band at 1 692 cm$^{-1}$.

7H-*Indeno*[1,2-a]*phenanthrene* (11).—2-Benzylidene-3,4-dihydrophenanthren-1(2*H*)-one [m.p. 130° (lit.,[13] 127—128°)] (1.0 g) was heated with polyphosphoric acid (30.0 g) at 150—160 °C for 3 h. The red mass was decomposed with ice–water, the organic matter thoroughly extracted with ether, and the extract washed successively with aqueous 10% sodium hydroxide and water, dried ($Na_2SO_4$), and evaporated. The residual gum was adsorbed on a column of neutral alumina and eluted with petroleum. The first few fractions gave gummy material which was rejected. 7*H*-Indeno[1,2-*a*]phenanthrene (11) was finally obtained from the later eluates as a crystalline solid (100 mg), m.p. 188—189° (petroleum) (lit.,[13] m.p. 189°) (Found: C, 94.5; H, 5.4 Calc. for $C_{21}H_{14}$: C, 94.7; H, 5.3%); $\lambda_{max.}$ (EtOH) 224 (log ε 4.59), 265 (4.40), 280 (4.23), 300 (4.15), 311 (4.29), 325 (4.10), 343 (3.60), and 356 (3.41); $\lambda_{min.}$ 240 (4.08), 275 (4.20), 291 (4.00), 302 (4.13), 320 (4.08), 340 (3.40), and 353 (3.06); τ ($CDCl_3$; 100 MHz) 1.12—1.34 (3 H, m, 4- + 5- + 12-H), 1.50 (1 H, d, *J* 8 Hz, 13-H), 1.96—2.20 (3 H, m, 1- + 11- + 6-H), 2.24—2.48 (3 H, m, 2- + 3- + 8-H), 2.60—2.76 (2 H, m, 9- + 10-H), and 5.95 (2 H, s, 7-$H_2$). The 2,4,7-*trinitrofluorenone complex* was prepared in benzene–ethanol and purified from the same solvent as a red amorphous powder, m.p. 203° (Found: C, 70.0; H, 2.95; N, 7.0. $C_{34}H_{19}N_3O_7$ requires C, 70.2; H, 3.3; N, 7.2%).

*Diels Hydrocarbon.*—The Diels hydrocarbon, m.p. 226°, was prepared from cholesterol according to the method of Diels *et al.*[2] Other indeno[2,1-*a*]phenanthrenes and their derivatives were available from preivous work.[10,14]

*Mass Spectra.*—The mass spectrum of the Diels hydrocarbon showed peaks at *m/e* 336 ($M^+$, 100%), 293 ($M - C_3H_7$, 40), 279 ($M - C_4H_9$, 27), and 278 (22) [$M$ * 255.5 (336 ⟶ 293) and 231.7 (336 ⟶ 279). 7-Isobutyl-9-methyl-11*H*-indenophenanthrene (8) showed *m/e* 336 ($M^+$, 100%), 293 ($M - C_3H_7$, 95), 279 ($M - C_4H_9$, 20), and 278 (28) [$M$ * 255.5 (336 ⟶ 293) and 231.7 (336 ⟶ 279)].

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[26] W. E. Bachmann, J. W. Cook, C. L. Hewett, and J. Iball, *J. Chem. Soc.*, 1936, 54.