The Structure of the Product from Reaction of an Equimolar Mixture of 1- and 2-Bromomethylnaphthalenes with Enneacarbonyldi-iron. A New π-Complex with a Trimethylenemethane-type Ligand

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Summary The product of reaction of an equimolar mixture of 1- and 2-bromomethylnaphthalenes with $Fe_2(CO)_9$ is a new π-complex with a trimethylenemethane ligand which constitutes a part of the 2-naphthylmethyl group, the latter being alkylated in the 4-position of its co-ordinated benzene ring by the 1-naphthylmethyl radical, which does not participate in co-ordination with the iron atom.

Recently it was reported[1] that an interaction of 2-bromomethylnaphthalene with $Fe_2(CO)_9$ gives a complex $(C_{10}H_7CH_2)_2Fe(CO)_3$ (I). We have studied a reaction of $Fe_2(CO)_9$ with a 1 : 1 mixture of 1- and 2-bromomethylnaphthalenes, which gave the crystalline compound (II), m.p. 102°, with the same composition as (I). We report the results of an X-ray study of compound (II), showing that it is a new trimethylenemethane π-complex. To elucidate the structure of (I) we have also undertaken an X-ray investigation of its well crystallized bromo-derivative.

The yellow prismatic crystals of (II) belong to the monoclinic space group $P2_1/c$ with unit-cell parameters: $a = 8{\cdot}36 \pm 0{\cdot}03$, $b = 17{\cdot}63 \pm 0{\cdot}02$, $c = 13{\cdot}73 \pm 0{\cdot}02$ Å, $\beta = 95° \pm 1°$ $D_m = 1{\cdot}40$, $D_c = 1{\cdot}4$ g.cm^{-3} for $Z = 4$, $M = 422{\cdot}27$. Intensities of *ca.* 1500 independent non-zero reflections were estimated visually, disregarding absorption corrections, from Weissenberg photographs taken with unfiltered copper radiation. The structure was solved by a combination of Patterson, Fourier, and isotropic full-matrix least-squares refinement procedures. The present discrepancy index is $R_F = 13\%$ with an overall temperature factor $B = 5{\cdot}5$ Å^2. Standard deviations in bond lengths are 0·02 for Fe–C, 0·03 for C–O and 0·04 Å for C–C; those in bond angles are 2—3°.

The molecular structure is shown in the Figure. Apart from the three carbonyl groups, the iron atom is co-ordinated only by the 2-naphthylmethyl group, specifically by its trimethylenemethane fragment. The 1-naphthylmethyl residue, which is incapable of such co-ordination, has alkylated the 2-naphthylmethyl moiety in the 4-position of its co-ordinated benzene nucleus. The iron atom co-ordination is very similar to that found in phenyltrimethylenemethaneiron tricarbonyl $[(CH_2)_2C(CHPh)]Fe(CO)_3$ (III), the first trimethylenemethane π-complex studied by X-ray diffraction.[2] The iron atom is located directly beneath the central carbon atom C(4) of the trimethylenemethane ligand. The Fe–C(4) distance is significantly shorter than other three distances involving the π-bonded carbon atoms: Fe–C(4) 1·95, –C(5) 2·10, –C(6) 2·11, –C(14) 2·11 Å [in (III) the corresponding distances are 1·932, 2·098, 2·118, and 2·169 Å]. The iron atom co-ordination is octahedral and the trimethylenemethane ligand and the $Fe(CO)_3$ moiety adopt a mutually staggered conformation. Carbon–carbon distances within the trimethylenemethane moiety are similar to those found in (III). Its bond angles [C(5)C(4)C(6) 116°, C(6)C(4)C(14) 108°, C(14)C(4)C(5) 119°] show that this ligand is nonplanar. The central atom C(4) is displaced by 0·26 Å away from the iron atom relative to the plane passing through C(5), C(6), and C(14) [in (III) this displacement is 0·315 Å]. Due to co-ordination with the iron atom and to alkylation by the 1-naphthylmethyl radical the corresponding benzene nucleus of the 2-naphthylmethyl residue has lost its aromaticity and planarity. Deviations from the plane of the second benzene ring C(7) ··· C(12), which remains essentially planar and aromatic, are: C(13) 0·04, C(6) 0·07, C(14) 0·11, C(4) −0·32, C(5) −0·12, and C(15) −1·29 Å. The C(13) atom becomes tetrahedral, and the C(13)–C(14) and C(13)–C(12) distances correspond to single bonds. Probably because of rather large standard errors the C(6)–C(7) and Fe–C(6) distances are shorter than they ought to be, *cf.* ref. 2.

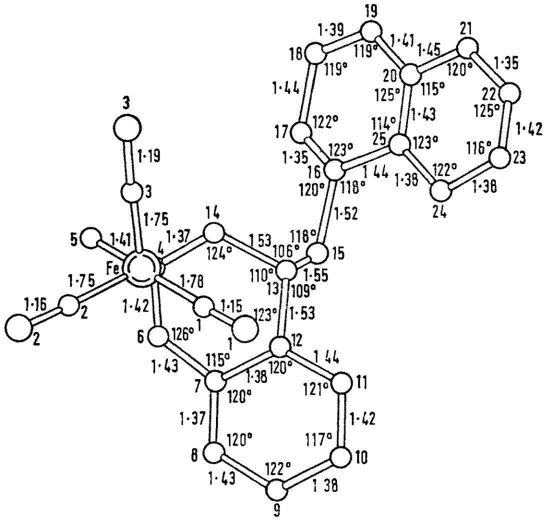

Figure. *The molecule projected on to the plane defined by* C(7) · · C(12) (*the planar benzene ring*).

The non-co-ordinated 1-naphthylmethyl residue is planar, including the bridging methylene group $C(15)H_2$. Its bond lengths are similar to those found in the structure of naphthalene itself.[3]

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[1] A. N. Nesmeyanov, I. I. Kritskaya, G. P. Zol'nikova, Yu. A. Ustynyuk, G. M. Babakhina, and A. M. Vainberg, *Doklady Akad. Nauk S.S.S.R.*, 1968, **182**, 1091.

[2] M. R. Churchill and K. Gold, *Inorg. Chem.*, 1969, **8**, 401.

[3] D. W. J. Cruickshank, *Acta Cryst.*, 1958, **10**, 693.