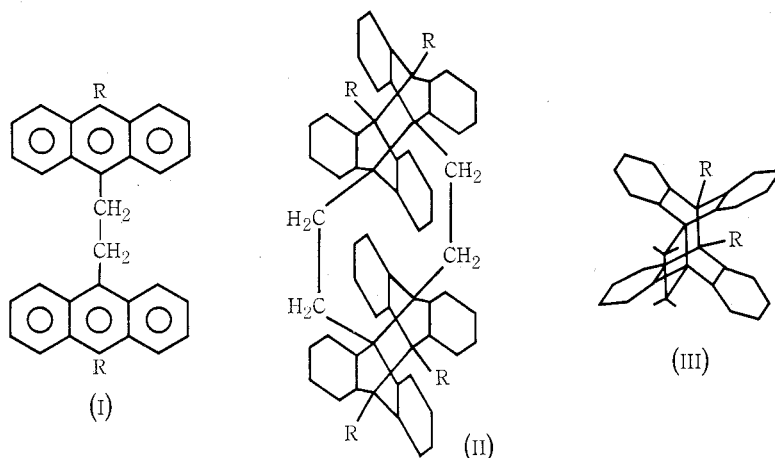


DIANTHRACENE ISOMERS OF 1,2-BIS(10'-ALKYL-9'-ANTHRYL)ETHANES*

By F. H. C. STEWART†

In 1952 Roitt and Waters¹ synthesized 1,2-bis(9'-anthryl)ethane (I; R = H) by the action of free radicals on 9-methylantracene. The fluorescent product (I; R = H) was accompanied by a small amount of a colourless, non-fluorescent material with the same empirical composition. This substance was also formed by ultraviolet irradiation of (I; R = H), and was assigned the dimeric structure (II; R = H) in which pairs of anthracene nuclei are joined covalently at the 9'- and 10'-positions as in dianthracene, the photodimer of anthracene itself.²



Some years later Stewart³ prepared several 1,2-bis(9'-anthryl)ethanes (I) by treatment of 9-chloromethylantracenes with methylmagnesium iodide. In addition to the unsubstituted compound (I; R = H), the methyl (I; R = CH₃), n-butyl (I; R = C₄H₉), and dodecyl (I; R = C₁₂H₂₅) derivatives were obtained in this way. In each case the main product (I) was accompanied by a small quantity of the so-called "photodimer". Irradiation of the n-butyl compound (I; R = C₄H₉) by sunlight gave the same product as that produced in the Grignard coupling.³

It was pointed out at the time (1961) that the evidence for the dimeric structure (II; R = H) advanced by Roitt and Waters¹ was inconclusive, and did not preclude

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† Division of Protein Chemistry, CSIRO Wool Research Laboratories, Parkville, Vic. 3052.

¹ Roitt, I. M., and Waters, W. A., *J. chem. Soc.*, 1952, 2695.

² Coulson, C. A., Orgel, L. E., Taylor, W., and Weiss, J., *J. chem. Soc.*, 1955, 2961.

³ Stewart, F. H. C., *Aust. J. Chem.*, 1961, **14**, 177.

the monomeric cyclobutane arrangement (III; R = H) arising from intramolecular formation of the dianthracene system. Molecular weight determinations on the "photodimer" of (I; R = H) by the Rast method, however, were vitiated owing to reversion to the parent bisanthrylethane (I; R = H) at elevated temperatures.¹

Livingston and Wei⁴ reported recently that the application of various physical techniques, including molecular weight determination by vapour pressure osmometry, demonstrates that the "photodimer" of 1,2-bis(9'-anthryl)ethane (I; R = H) has, in fact, the monomeric structure (III; R = H). It was of interest, therefore, to ascertain if the alkyl-substituted products from the Grignard coupling reactions also adopted the same, rather strained, monomeric structure (III) instead of the dimeric form (II). For this purpose, the molecular weights of the n-butyl and dodecyl compounds have now been measured by vapour pressure osmometry.*

The values obtained were 466 (calc. 494 for monomer, 988 for dimer) with the n-butyl derivative, and 694 (calc. 738 for monomer, 1476 for dimer) with the dodecyl analogue, respectively. For solubility reasons it was necessary to use very dilute solutions, and consequently a high degree of accuracy could not be attained. The dodecyl compound, moreover, and to a lesser extent the n-butyl derivative, crystallized slowly from solution, and the observed molecular weights decreased with time. It is evident from the results, however, that both alkyl-substituted compounds are monomeric, and presumably have the cyclobutane structure (III) discussed by Livingston and Wei.⁴

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* The measurements were carried out at 37° in freshly prepared benzene solutions ($\approx 0.2\%$) using a Mechrolab 301A vapour pressure osmometer. The solvent was calibrated with benzil. Absence of visible fluorescence in the solutions during and immediately after the determinations indicated that formation of the parent, highly fluorescent bis(9'-anthryl)ethanes did not occur to any significant extent. On prolonged standing, however, distinct blue fluorescence developed in the solutions.

⁴ Livingston, R., and Wei, K. S., *J. Am. chem. Soc.*, 1967, **89**, 3098.