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FULVENES AND THERMOCHROMIC ETHYLENES. PART 35[1]. THE N. M. R. SPECTRUM AND THE SPATIAL STRUCTURE OF DIBIPHENYLENEËTHENE

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The problem of the detailed spatial structure of dibiphenyleneëthene (I) has been studied repeatedly, both theoretically and experimentally, but no definite solution has been reached. The combination of two features makes it difficult to arrive at a prediction of the structure: the "fulvenic" nature of the central double bond, which expresses itself in its unusual chemical reactions[2), in the unusual distortion polarization[3), and in the unusual bond order found in LCAO calculations[4); and - on the other hand - the "overcrowding" of the molecule, in which the four hydrogen atoms in the positions 1, 1', 8, 8', interfere with the planar structure that would otherwise result from the presence of a normal double bond in the centre of the molecule. This inconsistency is thrown into relief by a comparison of dibiphenyleneëthene (I) with the thermochromic ethylenes such as dixanthylene and bianthrone, in which the overcrowding resembles that prevailing in I, whilst the central double bond has no fulvenic character: dixanthylene and bianthrone exist in a colorless and a colored modification, whilst only one, red, form of I is known.

In the solid state, dibiphenyleneëthene (I) is not monoplanar; the benzene rings are bent out of the plane of the central fulvalene system, but without sacrificing the centrosymmetry of the molecule[5)]. In order to obtain information on the spatial structure of I in solution, we have applied nuclear magnetic resonance spectroscopy to this hydrocarbon, expecting the results to be interpretable without reference to any preconceived structural hypothesis.

In deuterocholoroform as solvent, three distinct multiplets have been observed in the following ratio:

$$2.79\tau : 2.39\tau : 1.69\tau = 2 : 1 : 1$$

We submit that the assignment of these three multiplets to the eight hydrogen atoms in 2, 3, 6, 7, 2', 3', 6', 7' -, the four hydrogen atoms in 4, 5, 4', 5' -, and the four hydrogen atoms in 1, 8, 1', 8', respectively, is unequivocal. The assignment follows from the comparison of the N. M. R. spectrum of I with that of 2, 7, 2', 7' - tetramethyl-dibiphenyleneëthene (II) and dibiphenylene-ethane (III). In II, one observes a singlet at 4.0 τ, a singlet at 1.77 τ, a doublet at 2.44 τ, and another doublet at 2.85 τ. The ratio of the four peaks is 6 : 2 : 2 : 2 ; the peak at 4.0 τ is undoubtedly due to the methyl hydrogen atoms. In III, which lacks the central double bond, one finds an aliphatic singlet at 5.29 τ and two aromatic multiplets at 2.39 τ and 2.89 τ; the ratio between the peaks is 1 : 2 : 6, respectively. The absorption in the low field, which is so characteristic of I and II, is absent in III[6)].

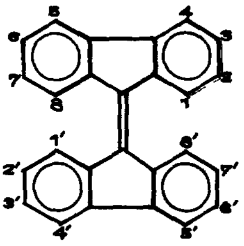
The comparison of the spectra of I and II proves that the multiplet at 2.79 τ in I corresponds to the hydrogen atoms 2, 3, 6, 7, 2', 3', 6', 7' and the doublet at 2.85 τ in II to the hydrogen atoms in 3, 6, 3', 6'. The important difference between the spectra of I and II lies, therefore, in the fact that in the former we have a multiplet in the low field (at 1.69 τ), in the latter a singlet (at 1.77 τ). Only the hydrogen atoms at 1, 1', 8, 8' can give such a singlet: the methyl groups at 2, 7, 2', 7' in II prevent the splitting at the neighboring position which is, of course, possible in I. The doublet at 2.44 τ in II is, then, related to the hydrogen atoms at 4, 4', 5, 5', which appear - as expected - in I and III as multiplets.

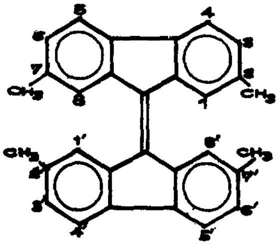
It is thus clear that in the N. M. R. spectrum of dibiphenyleneëthene, there appears a distinct absorption in the low field due to the four hydrogen atoms that crowd the central double bond. We submit that this absorption in the low field reflects an interaction between these four hydrogen atoms[7), especially in view of the fact[6) that the closely analogous, but conformationally more mobile 9-benzhydrylidenefluorene does not show an analogous effect. No conclusion can yet be drawn from these data as to the exact spatial structure of I.

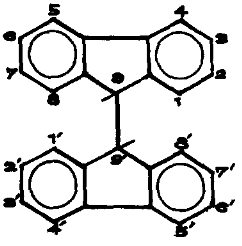
The exact distance between these hydrogen atoms, that would still permit interaction, will have to be determined by other means[8). However, it can already be said that if the dibiphenyleneëthene molecule is twisted, as has been concluded, e. g., from its absorption spectrum[9), the twist must be limited to a degree which still permits interaction between the "ortho"-hydrogen atoms. In this connection, it should be noted that dixanthylene in its colorless form does not indicate any interaction between the "ortho"-hydrogen atoms in its N. M. R. spectrum[10).

The results obtained invite a study of other overcrowded ethylenes, such as dixanthylene and bianthrone, and of other fulvenes[11). This study is now in hand.

Chart I







I	II	III
multiplet at 1.69 τ (hydrogen atoms at 1, 8, 1', 8')	singlet at 1.77 τ (hydrogen atoms at 1, 8, 1', 8')	
multiplet at 2.39 τ (hydrogen atoms at 4, 5, 4', 5')	doublet at 2.44 τ (hydrogen atoms at 4, 5, 4', 5')	multiplet at 2.39 τ (hydrogen atoms at 4, 5, 4', 5')
multiplet at 2.79 τ (hydrogen atoms at 2, 3, 6, 7, 2', 3', 6', 7')	doublet at 2.85 (hydrogen atoms at 3, 6, 3', 6')	multiplet at 2.89 τ (hydrogen atoms at 1, 2, 3, 6, 7, 8, 1', 2', 3', 6', 7', 8')
	singlet at 4.0 τ (methyl hydrogen atoms)	
		singlet at 5.29 τ (hydrogen atoms at 9, 9')

REFERENCES

1. Part 34: E. D. Bergmann and I. Agranat, J. Am. Chem. Soc., 86, 3587 (1964).
2. Reaction with lithium aluminum hydride: D. Lavie and E. D. Bergmann, Bull. Soc. chim. France, 18, 250 (1951). Reduction potential: S. Wawzonek and J. W. Fan, J. Am. Chem. Soc., 68, 2541 (1946)
3. E. D. Bergmann, E. Fischer and J. H. Jaffe, J. Am. Chem. Soc., 75, 3230 (1953).

4. E. D. Bergmann, G. Berthier, A. Pullman and B. Pullman, Bull. Soc. chim. France, 17, 1079 (1950).
5. S. C. Nyburg, Acta Cryst., 7, 779 (1954).
6. This absorption is also absent in 9-benzylidenefluorene, 9-benzhydrylidenefluorene and tetraphenylethylene, which we have studied in parallel (unpublished results).
7. The interaction of hydrogen atoms in other overcrowded molecules has recently been studied by Martin and co-workers: R. H. Martin, N. Defay, F. Geerts-Evrard and S. Delavarenne, Tetrahedron, 20, 1073 (1964).
8. An interesting experimental possibility is the measurement of the dipole moment of suitably substituted dibiphenyleneäthenes. The moment of 2, 2' - difluorodibiphenyleneäthene has been measured (E. D. Bergmann, J. Chem. Soc., 987 (1935); it is different from 0, so that the molecule cannot be the planar *trans*-form, but smaller than the moment calculated for the *cis*-form, and seems thus to indicate a twisted configuration. (For other dipole measurements, see E. Bergmann and E. Fischer, Bull. Soc. chim. France, 17, 1084 (1950); 19, 712 (1952). This question is now being studied further, also in the light of the observation that dibiphenyleneäthene shows a very high (30 - 40 cm^3) distortion polarization[3].
9. See, e. g., E. D. Bergmann in "Progress in Organic Chemistry", Vol. 3 (Butterworths Scientific Publication, London, 1955), p. 133. Cf. R. S. Mulliken and C. C. Roothann, Chem. Revs., 41, 219 (1947).
10. Unpublished work from this laboratory.
11. Recently the N. M. R. spectrum of three simple fulvenes has been studied by W. B. Smith and B. A. Shoulders, J. Am. Chem. Soc., 86, 3118 (1964).