227. *Dipole Moment and Molecular Structure. Part XIV.** 2 : 2′-*Difluorobisdiphenylene-ethylene.*

By Ernst Bergmann.

Hitherto only one of the two theoretically possible geometrical isomerides has been detected in the fulvene series, *e.g.*, in 2 : 2′-disubstituted bisdiphenylene-ethylenes, (I) and (II); and it is of interest to determine whether this has the *cis*- or the *trans*-configuration. If the

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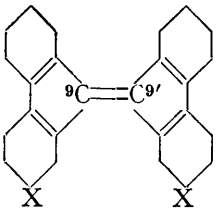
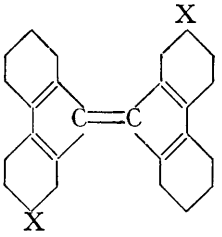
substituents X are polar, one would expect (II) to be more favoured. A convenient method for deciding the question is the measurement of the dipole moment, since for (I) this is equal to the sum of the substituent moments, whereas for (II) it is equal to their difference,



(I; *cis*-.)



(II; *trans*-.)

i.e., zero in this case. [The small deformation of the diphenyl system caused by the ring closure of the fluorene nucleus (Mills, Palmer, and Tomkinson, J., 1924, **125**, 2365; Bergmann, Engel, and Hoffmann, *Z. physikal. Chem.*, 1932, *B*, **17**, 95) may be neglected here, since it does not markedly affect the values.]

2 : 2′-Dinitrobisdiphenylene-ethylene (Bergmann, Hoffmann, and Winter, *Ber.*, 1933, **66**, 46) and some analogous substances were too sparingly soluble in non-polar solvents, but the 2 : 2′-*difluoro*-compound was suitable. It was readily synthesised by the action of molecular silver on a boiling xylene solution of 9 : 9-dichloro-2-fluorofluorene. Its dipole moment was 2·51, decidedly nearer to that of the *cis*-configuration, which requires 2·90 = 2 × 1·45 (Bergmann, Engel, and Sandor, *Z. physikal. Chem.*, 1930, **10**, 106; the data of Bergmann, Engel, and Hoffmann, *loc. cit.*, show that the substituent moments of such compounds are not seriously affected by the trunk of the molecule). This result is rather surprising, but is in unison with the facts that *cis*- is more stable than *trans*-dichloroethylene (Ebert and Buell, *Z. physikal. Chem.*, 1931, *A*, **152**, 451) and that the diarylmaleic acids have a lower energy content than the corresponding fumaric compounds (Ramart-Lucas and Hoch, *Compt. rend.*, 1926, **189**, 696).

Experimental.

The determination of the electronic polarisation (P_E) for highly coloured substances could not be carried out in the usual way, partly because of the impossibility of evaluating the refractive index of their solutions with the Zeiss interferometer, and partly because the electronic polarisation is strictly equal to the molecular refraction only for colourless substances. Therefore (cf. Bergmann, Engel, and Sandor, *Ber.*, 1930, **63**, 2572) we determined the total polarisation (P) of the unsubstituted bisdiphenylene-ethylene, in which, since there is no electric moment, P depends solely on the electronic polarisation. (The atomic polarisation, P_A, is neglected, as usual, for our comparison purposes; it is, moreover, theoretically reasonable to do so.) Subtraction of the refractive equivalent for two hydrogen atoms and addition of that for two fluorine atoms (0·997; Schiemann, *Naturwiss.*, 1931, **19**, 706; *Z. physikal. Chem.*, 1931, *A*, **156**, 387) gives the desired P_E for the fluoro-compound, *viz.*, 109·76.

In the following table, c is the molar fraction, M the average molecular weight, ρ the density, ε the dielectric constant, P_1 the total polarisation of the solution, P the total polarisation of the solute, and P_0 the orientation polarisation, which is extrapolated graphically for infinite dilution (P_0^∞).

Bisdiphenylene-ethylene in benzene; $t = 16{\cdot}0°$.

c.	M.	ρ.	ϵ.	P_1.	P.	P_0.
0	78	0·8833	2·2920	26·5806	—	—
0·01447	81·617	0·9061	2·3384	27·7881	110·03	(0)
0·01854	82·634	0·9125	2·3518	28·1307	110·20	(0)
0·02252	83·629	0·9188	2·3641	28·4507	109·64	(0)

2 : 2′-*Difluorobisdiphenylene-ethylene in benzene*; $t = 14{\cdot}7°$.

0	78	0·8849	2·2946	26·5706	—	—
0·00725	80·072	0·8905	2·3649	28·1181	240·16	130·02
0·00959	80·741	0·8962	2·3824	28·4187	219·37	109·41
0·01201	81·435	0·8991	2·4064	28·9087	221·24	111·28

$P_0^\infty = 135$; $\mu = 2{\cdot}51$.

Synthesis of 2 : 2′-*Difluorobisdiphenylene-ethylene.*—9 : 9-Dichloro-2-fluorofluorene (1·5 g.) was heated with silver powder (3·75 g.) in xylene (20 c.c.) for 12 hours, the filtered solution evaporated in a vacuum, and the crystalline residue (0·8 g.) twice recrystallised from amyl alcohol; fine red needles, m. p. 226—227°; yield 0·5 g. (Found : C, 86·0; H, 4·0. $C_{26}H_{14}F_2$ requires C, 85·7; H, 3·9%). The occurrence of traces of this substance has already been observed by Bergmann, Hoffmann, and Winter (*loc. cit.*) in similar experiments.

Bisdiphenylene-ethylene.—9 : 9-Dichlorofluorene (14 g.) and copper-bronze (28 g.; " Naturkupfer C ") were heated in benzene (200 c.c.) for 20 hours, and the product worked up as before; yield 3·3 g.; m. p. 189° (see Schmidt and Wagner, *Ber.*, 1910, **43**, 1796).

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