Phys. Org.

Fulvenes and Thermochromic Ethylenes. Part LX.¹ The Conformation of 5H-Dibenzo[a,d]cyclohepten-5-one and 10,11-Dihydro-5H-dibenzo-[a,d]cyclohepten-5-one

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The monochloro- and dichloro-derivatives of 5H-dibenzo[a,d]cyclohepten-5-one and 10,11-dihydro-5H-dibenzo-[a,d] cyclohepten-5-one have been synthesised. Dipole moments of the compounds show that their molecules cannot be planar.

BERGMANN and his co-workers² concluded that the molecules of 5H-dibenzo[a,d]cycloheptene (I) and 10,11-dihydro-5H-dibenzo[a,d]cycloheptene (II) are not planar, a view supported by some workers but disclaimed by others.³⁻⁶ We have studied this problem by measuring the dipole moments of 5H-dibenzo[a,d]cyclohepten-5-one 10,11-dihydro-5*H*-dibenzo[*a*,*d*]cyclohepten-5-one (IV), and some of their chloro-derivatives (V)--(VIII). The experimental results are summarised in the Table.

† This work forms part of the Ph.D. Thesis of A. Solomonovici, to be submitted to the Hebrew University of Jerusalem.

¹ Part LIX, E. D. Bergmann and I. Agranat, J. Chem. Soc. (C), 1971, 1541. Preliminary communication, I. Agranat, H.Weiler-Feilchenfeld, and R. M. J. Loewenstein, Chem. Comm., 1970, 1153.
² E. D. Bergmann, E. Fischer, D. Ginsburg, Y. Hirshberg,

D. Lavie, M. Mayot, A. Pullman, and B. Pullman, Bull. Soc. chim. France, 1951, 18, 684.

E. D. Bergmann, Progr. Org. Chem., 1955, 3, 81.
E. D. Bergmann, Chem. Rev., 1968, 68, 41.
A. Julg, J. Chim. phys., 1962, 59, 759.

If it is assumed that these compounds are planar and that all the rings are regular polygons, the expected dipole moments of the halogen derivatives can be



⁶ Z. Aizenshtat, Ph.D. Thesis, Hebrew University, Jerusalem, 1969.

calculated vectorially, from $\mu_{C-CI} = 1.58 \text{ D}^7$ and from the experimental values of the parent ketones [2.96 D for (III) and 3.32 D for (IV)]. The moments thus obtained appear in the Table as $\mu_{calc.}$, together with the

Experimental dipole moments (in benzene, at 30°)

			μ (D)			
α΄	β'	$P_{2^{\infty}}$	$R_{\mathtt{M}}$	Found	Calc.	$\Delta \mu$ (d)
15.84	-0.83	287.06	65.90	3.32		
25.83	-1.10	440.67	77.09	4.25	4.54	-0.29
24.53	-1.60	421.75	72.04	4.17	5.62	-1.45
13.54	-0.92	250.05	71.51	2.98 *		
19.23	-1.13	341.26	74.99	3.64	4.19	-0.55
20.44	-1.64	359.26	83.52	3.70	5.28	-1.58
	α' 15.84 25.83 24.53 13.54 19.23 20.44	$\begin{array}{cccc} \alpha' & \beta' \\ 15.84 & -0.83 \\ 25.83 & -1.10 \\ 24.53 & -1.60 \\ 13.54 & -0.92 \\ 19.23 & -1.13 \\ 20.44 & -1.64 \end{array}$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	$\begin{array}{c cccccc} & & & & & & & & & & & \\ \alpha' & \beta' & P_{2\infty} & R_{\rm M} & {\rm Found} & {\rm Calc.} \\ 15\cdot84 & -0\cdot83 & 287\cdot06 & 65\cdot90 & 3\cdot32 \\ 25\cdot83 & -1\cdot10 & 440\cdot67 & 77\cdot09 & 4\cdot25 & 4\cdot54 \\ 24\cdot53 & -1\cdot60 & 421\cdot75 & 72\cdot04 & 4\cdot17 & 5\cdot62 \\ 13\cdot54 & -0\cdot92 & 250\cdot05 & 71\cdot51 & 2\cdot98 & * \\ 19\cdot23 & -1\cdot13 & 341\cdot26 & 74\cdot99 & 3\cdot64 & 4\cdot19 \\ 20\cdot44 & -1\cdot64 & 359\cdot26 & 83\cdot52 & 3\cdot70 & 5\cdot28 \end{array}$

* An earlier determination of this moment gave 2.94 D (T. Billé-Samé, Ph.D. Thesis, Hebrew University, Jerusalem, 1969) and the mean value of 2.96 D was used in the calculations.

experimental figures μ_{found} and the difference $\Delta \mu$ defined as $\mu_{\text{found}} - \mu_{\text{cale}}$. In the monohalogenated compounds the differences $\Delta \mu$ are relatively small and may not be



The Dreiding model of (VII) (the small sphere represents the oxygen atom, the large spheres represent the two chlorine atoms)

significant; they could be explained by a deviation of the rings from regularity. In the dichloro-derivatives, however, these differences are considerable (of the order of 1.5 D).

It is thus clear that these molecules cannot be planar. One may conclude that this is also true for the monohalogenated ketones: indeed the Dreiding models of all these compounds are nonplanar.

Calculations of the angle between the C=O and the C-Cl bonds from the observed moments of the monohalogeno-derivatives gives values of 77 and 64° for (V) and (VI) respectively; these are in reasonable agreement with the angles of *ca*. 75 and 65° that one observes on Dreiding models of these two molecules.

The results obtained for the dichloro-derivatives are more difficult to interpret unequivocally. If these molecules are not planar, both the angle between the two C-Cl group moments and the angle between their resultant and the C=O group moment are undetermined; an infinite number of sets of two values, all in agreement with the experimental moments, can be given for these

⁷ C. P. Smyth, ' Dielectric Behaviour and Structure,' McGraw-Hill, 1955, p. 253. angles. In the Dreiding model (Figure) the two C-Cl bonds are at an angle of $ca. 75^{\circ}$ to each other and their resultant is practically perpendicular to the C=O bond. With these angles, vector addition of the group moments gives a calculated moment of 3.85 D for the dichloro-trienone (VII) and 4.16 D for the dichloro-dienone (VIII), values which are close enough to the experimental ones to show that this model is able to account for the observed moments of the molecules. The study of the dipole moments therefore confirms the view that these molecules are not planar.

EXPERIMENTAL

Synthetic Methods.—The monochloro-ketones (V) and (VI) were synthesised by a literature method ⁸ and had the following physical constants: (V), m.p. 106—108° (from PrⁱOH) (lit.⁸ 109—111°); λ_{max} (EtOH) 314 nm. (log $\varepsilon 4.14$), $\bar{\nu}_{max}$ (KBr) 1640 cm.⁻¹; (VI), b.p. 175—178°/0.5 mm. (lit.⁸ 146—148°/0.05 mm.), m.p. 64—65° (from hexane) (lit.⁸ 65—66°), λ_{max} (EtOH) 269 nm. (log $\varepsilon 4.16$), $\bar{\nu}_{max}$ (KBr) 1640 cm.⁻¹.

The dichloro-ketones, (VII) and (VIII), were prepared in a similar way to (V) and (VI) by the condensation of 4-chlorophthalic anhydride with p-chlorophenylacetic acid. The resulting 2-(p-chlorobenzylidene)-5-chlorophthalide (IX) was reduced with hydriodic acid to give 2-(p-chloro- β -phenethyl)-5-chlorobenzoic acid (X). By decarboxylation of (X), 4,4'-dichlorobibenzyl (XI) was obtained. The last reaction is consistent with the assignment of structure (IX) to the compound; it excludes the isomeric condensation product (IXa) which would have given 3,4'-dichlorobibenzyl (XIa). Dehydrocyclisation of (X) by polyphosphoric acid yielded (VIII), and (VII) was obtained by further photodehydrogenation of (VIII) by bromine.

2-(p-Chlorobenzylidene)-5-chlorophthalide (IX).-4-Chlorophthalic anhydride was prepared from the commercial







sodium salt of 4-chlorophthalic acid by heating the free acid (40 g.) (m.p. $156-157^{\circ}$) at 160° for 5 hr. The product solidified when cool and gave colourless crystals (30 g., 83%) from benzene-light petroleum (2:1), m.p. $95-96^{\circ}$ (lit.⁹ $96-97^{\circ}$).

⁸ S. O. Winthrop, M. A. Davis, G. S. Myers, J. G. Gavin, R. Thomas, and R. Barber, *J. Org. Chem.*, 1962, 27, 230.

⁹ A. Rée, Annalen, 1886, **233**, 216.

A mixture of 4-chlorophthalic anhydride (27.5 g.), p-chlorophenylacetic acid (34 g.), and freshly fused sodium acetate (1 g.) was heated under reflux at 240° for 3 hr. The product crystallised from ethanol as yellowish crystals, (21.5 g., 50%); after recrystallisation from ethanol it had m.p. 209—210°, λ_{max} (EtOH) 316 (log ε 5.05) and 342 nm. (5.04); \bar{v}_{max} (KBr) 1765, 1610, 1500, 1440, 1290, 990, 820, 760, and 690 cm.⁻¹ (Found: C, 61.7; H, 3.0; Cl, 24.4. Calc. for $C_{15}H_8Cl_2O_2$: C, 61.9; H, 2.8; Cl, 24.4%).

2-(p-Chloro-\beta-phenethyl)-5-chlorobenzoic Acid (X).—A mixture of compound (IX) (20.5 g.) and hydriodic acid (120 ml.) was heated under reflux for 12 hr.; after a further 12 hr. at room temperature the mixture was poured onto crushed ice (500 g.) and the solid product was collected, dissolved in a boiling 25% solution of ammonia, filtered, and reprecipitated with 35% hydrochloric acid. Recrystallisation from cyclohexane gave almost colourless crystals $(10.8 \text{ g.}, 52\%), \text{m.p.} 138-140^{\circ}; \lambda_{\text{max.}}$ (EtOH) 268 (log $\varepsilon 3.08$), 276 (3.17), and 287 nm. (3.15); $\bar{\nu}_{max}$ (KBr) 1700, 1600, 1500, 1460, 1255, 830, 810, 725, and 690 cm.⁻¹ (Found: C, 61.0; H, 4.1; Cl, 24.0. Calc. for $C_{15}H_{12}Cl_2O_2$: C, 61.0; H, 4.1; Cl, 24.1%).

4,4'-Dichlorobibenzyl (XI).---A mixture of compound (X) (1 g.), copper chromite (0.8 g.), and quinoline (25 ml.) was heated at 210-220° for 3 hr.; the mixture was then cooled and poured into 10% hydrochloric acid (75 ml.). The organic product was extracted with ether and the extract was washed with 10% sodium carbonate solution and water, and then dried and evaporated. The product was distilled in vacuo to give 4,4'-dichlorobibenzyl (XI) (0.7 g., 82%), b.p. 119-122°/0.2 mm. (lit.¹⁰ 120°/0.2 mm.); m.p. 99-100° (from EtOH) (lit.¹¹ 101°); λ_{max} (EtOH) 268 (log ε 2.92) and 277 nm. (2.88); ν_{max} . (KBr) 1500, 1415, 1092, 1020, 830, 802, 717, 636, and 529 cm.⁻¹ (Found: C, 67.0; H, 4.7; Cl, 28.2. Calc. for C₁₄H₁₂Cl₂: C, 66.9; H, 4.8; Cl, 28.3%). The Dichloro-ketone (VIII).--A mixture of the acid (X)

¹⁰ A. L. J. Beckwith and W. A. Waters, J. Chem. Soc., 1957, 1665.

(9 g.) and polyphosphoric acid (100 ml.) was stirred at 170° for 3 hr. after which crushed ice was added and the mixture was extracted with ether. The extract was washed with 5% sodium carbonate solution and water, dried, and concentrated; the residue was distilled, b.p. 177-185°/0.35 mm. and the distillate was recrystallised from hexane, m.p. 78—79°; λ_{max} (EtOH) 271 nm. (log ϵ 4·19); $\bar{\nu}_{max}$ (KBr) 1650, 1595, 1295, 1270, 845, and 785 cm.⁻¹ (Found: C, 65·1; H, 3·6; Cl, 25·9. Calc. for C₁₅H₁₀Cl₂O: C, 65·0; H, 3.6; Cl, 25.6%).

The Dichloro-ketone (VII).-The ketone (VIII) (3 g.) was heated at 130° and bromine (2.6 g.) was added slowly, whilst the mixture was irradiated with u.v. light. After 30 min. the temperature was raised to, and maintained at, 200° until no more hydrogen bromide was evolved. The light yellow product recrystallised from isopropyl alcohol had m.p. 176–177° (2·1 g., 70%); λ_{max} (EtOH) 316 nm. (log ε 4·14); $\bar{\nu}_{max}$ (KBr) 1640, 1590, 1270, 855, 800, and 770 cm.⁻¹ (Found: C, 65·2; H, 2·8; Cl, 26·0. Calc. for $C_{15}H_8Cl_2O: C, 65.4; H, 2.9; Cl, 25.8\%).$

Dipole Moments.--- The dipole moments were determined at $30.0 \pm 0.1^{\circ}$ in benzene (sodium dried AnalaR). The dielectric constant of the solutions was measured with a heterodyne beat apparatus (500 kc), the specific volume with a Sprengel-Oswald pycnometer, and the refractive index with a Bellingham and Stanley Pulfrich Refractometer. The dipole moments were computed according to Halverstadt and Kumler.¹² The slopes α' and β' of the curves representing the dielectric constant and the specific volume of the solutions as functions of the molar fraction of the solute, are given in the Table as well as the polarisations $P_{2\infty}$ and the molar refractions $R_{\rm M}$. No correction for atomic polarisations was made. The experimental error is ca. ± 0.03 D.

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¹¹ K. M. Johnston and G. H. Williams, J. Chem. Soc., 1960,

1168. ¹² I. F. Halverstadt and W. D. Kumler, J. Amer. Chem. Soc., 1942, 64, 2988.