11. *Molecular Polarisability: Phenylpolyenals and Diphenylpolyene Ketones.*

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By the use of anisotropic bond polarisabilities deduced from acetone, vinylidene dichloride, benzene, etc., together with the assumption that polarisability exaltations operate in directions where electromeric shifts are possible, it is shown that measurements of molar Kerr constants can be reconciled with an *s-trans*-conformation for cinnamaldehyde, *s-cis* for benzylideneacetophenone, mainly *s-trans,s-cis* for cinnamylideneacetophenone, *s-cis,s-cis* for dibenzylideneacetone, and *s-trans,s-cis,s-cis,s-trans* for dicinnamylideneacetone, provided that, in certain cases, the phenyl groups are twisted out-of-plane, around their 1,4-axes, by 20—30°. In benzophenone a twist of 41° for each phenyl group is indicated. An empirical connection appears to exist between polarisability exaltation and $\lambda_{max.}$ of the *K*-band in conjugated ketones.

This paper deals with the anisotropy of polarisability of eight molecules in which C=O and C=C bonds are in conjugation. Previous work on the C=C link in certain chloroethylenes [1] and on the $[-C=C-]_n$ chain in various $\alpha\omega$-diphenylpolyenes [2] has suggested that the exaltation of polarisability in the polyenes is both a directional property and one whose effects on molar Kerr constants can be roughly predicted by a number of empirical methods. How far these methods are applicable when the conjugated system incorporates a C=O group is here explored through aldehydes and ketones of types (I) and (II).

(I) $Ph{\cdot}[CH{=}CH]_n{\cdot}CHO$ $\qquad$ $Ph{\cdot}[CH{=}CH]_n{\cdot}CO{\cdot}[CH{=}CH]_m{\cdot}Ph$ (II)

Experimental

Solutes.—Commercial benzaldehyde was washed repeatedly with aqueous sodium carbonate, then with water, dried (Na_2SO_4), and distilled in oxygen-free nitrogen. Cinnamaldehyde (B.D.H.) was thrice distilled in nitrogen, under which gas both aldehydes were stored until required. Crotonaldehyde and cinnamaldehyde were condensed as described by Kuhn and Wallenfels,[3] but the orange-red solid produced, m. p. 185° (from benzene), gave incorrect analyses for carbon and hydrogen. Slow evaporation of a solution in benzene (4 weeks) effected an improvement and raised the m. p. to 191°. The carbon content was still 1% low (although that for hydrogen was satisfactory). However, the material was accepted for the present purposes since the impurities were most probably other polyenals having polarities and polarisabilities similar to those of 11-phenylhendecapentaenal. Benzophenone (B.D.H.), twice crystallised from ethanol, has m. p. 48—49°. Dibenzylideneacetone, prepared as in ref. 4 and crystallised three times from ethyl acetate, had m. p. 114°; dicinnamylideneacetone, prepared as for the previous compound, formed yellow needles, m. p. 142°. Benzylidene- and cinnamylidene-acetophenone had m. p. 58° and 102°, respectively, and were prepared by following the directions in ref. 5.

Solvent and Solutions.—Benzene has been the solvent throughout. Commercial "Benzol Cryst.," as available in Sydney, was shaken with concentrated sulphuric acid for 8 hr. and left in contact with the acid overnight. The process was repeated until no colour was given to the acid layer. This was followed by refluxing this product over aqueous sodium hydroxide for 8 hr., separating it, and distilling it from phosphorus pentoxide on to sodium wire over which the purified solvent was stored. For use with benzaldehyde or cinnamaldehyde it was freed from air by boiling, and saturated, while cooling, with dry nitrogen. Solutions were made up by weight in glass-stoppered flasks which, with the two aldehydes, were flushed

[1] Bramley, Le Fèvre, Le Fèvre, and Rao, *J.*, 1959, 1183.
[2] Bramley and Le Fèvre, *J.*, 1960, 1820.
[3] Kuhn and Wallenfels, *Ber.*, 1937, **70**, 1331.
[4] *Org. Synth.*, Coll. Vol. II, 1943, p. 167.
[5] *Org. Synth.*, Coll. Vol. I, 1941, p. 78.

TABLE 1.

Dielectric constants, densities, and values * of ΔB and Δn for solutions in benzene containing weight fractions w_2 of solute.

Solute: *Benzaldehyde.*

$10^6 w_2$	7451	16,503	20,944	35,385	42,754	49,689
ε_{12}	2·3390	2·4212	2,4609	2·5923	2·6629	2·7250
d_{12}	—	0·87621	0·87683	0·87891	0·8801	—
$10^4 \Delta n$	3	7	9	15	18	21
$10^6 w_2$	9763	15,794	27,584	36,351	44,527	49,232
$10^7 \Delta B$	0·216	0·365	0·626	0·823	0·972	1·079

whence $\sum\Delta\varepsilon/\sum w_2 = 9{\cdot}068$, $\sum\Delta d/\sum w_2 = 0{\cdot}1457$, $\sum\Delta n/\sum w_2 = 0{\cdot}042$, and $10^7\sum\Delta B/\sum w_2 = 22{\cdot}270$

Solute: *Cinnamaldehyde.*

$10^6 w_2$	6254	15,660	26,003	33,176	38,890	49,662
ε_{12}	2·3414	2·4445	2·5571	2·6365	2·6940	2·8158
d_{12}	0·87471	0·87618	0·87782	0·87895	0·87992	0·88143
$10^4 \Delta n$	7	16	27	34	39	50
$10^6 w_2$	2029	3855	5770	9564	10,186	12,239
$10^7 \Delta B$	0·128	0·242	0·367	0·606	0·628	0·789

whence $\sum\Delta\varepsilon/\sum w_2 = 10{\cdot}930_5$, $\sum\Delta d/\sum w_2 = 0{\cdot}1552$, $\sum\Delta n/\sum w_2 = 0{\cdot}1020$, and $10^7\sum\Delta B/\sum w_2 = 63{\cdot}24$.

Solute: *11-Phenylhendecapentaenal.*

$10^6 w_2$	52	127	165	222	309	339
ε_{12}	2·2730	2·2739	—	—	2·2757	—
d_{12}	$0{\cdot}87378_6$	$0{\cdot}87381_4$	—	$0{\cdot}87383_6$	$0{\cdot}87388_1$	—
$10^4 \Delta n$	0·4	0·7	1·7	2·0	—	2·7
$10^7 \Delta B$	0·024	—	0·080	0·108	0·148	0·161

whence $\sum\Delta\varepsilon/\sum w_2 = 10{\cdot}4_5$, $\Delta d = 0{\cdot}1658 w_2 + 614 w_2^2$, $\sum\Delta n/\sum w_2 = 0{\cdot}829$, and $10^7\sum\Delta B/\sum w_2 = 479{\cdot}3$.

Solute: *Benzophenone.*

$10^6 w_2$	5537	10,168	17,031	19,933	25,292	35,330
ε_{12}	—	—	2·3705	2·3857	2·4159	2·4718
d_{12}	0·87487	0·87572	0·87724	0·87772	0·87880	0·88077
$10^4 \Delta n$	5	9	16	18	23	32
$10^7 \Delta B$	0·010	0·018	0·035	—	0·059	0·093

whence $\sum\Delta\varepsilon/\sum w_2 = 5{\cdot}676$, $\sum\Delta d/\sum w_2 = 0{\cdot}1981$, $\sum\Delta n/\sum w_2 = 0{\cdot}090_9$, and $10^7\Delta B = 1{\cdot}486 w_2 + 32{\cdot}4 w_2^2$.

Solute: *Benzylideneacetophenone.*

$10^6 w_2$	4266	8263	13,297	15,731	21,890	30,204
ε_{12}	2·2956	2·3175	2·3426	2·3554	2·3870	—
d_{12}	0·87461	0·87540	0·87634	0·87682	0·87800	0·87962
$10^4 \Delta n$	7	13	20	24	32	—
$10^5 w_2$	2039	2246	2928	3639	4222	—
$10^7 \Delta B$	0·041	0·043	0·058	0·070	0·085	—

whence $\sum\Delta\varepsilon/\sum w_2 = 5{\cdot}289$, $\sum\Delta d/\sum w_2 = 0{\cdot}1934$, $\sum\Delta n/\sum w_2 = 0{\cdot}1513$, and $10^7\sum\Delta B/\sum w_2 = 1{\cdot}97$.

Solute: *Cinnamylideneacetophenone.*

$10^6 w_2$	2928	5393	8975	12,579	14,690	17,787
ε_{12}	2·2865	2·2973	2·3165	2·3334	2·3454	2·3618
d_{12}	0·87437	0·87482	0·87545	0·87613	0·87653	0·87707
$10^4 \Delta n$	6	11	18	25	29	35
$10^5 w_2$	1742	1965	2662	4567	—	—
$10^7 \Delta B$	0·094	0·109	0·148	0·251		

whence $\sum\Delta\varepsilon/\sum w_2 = 4{\cdot}906$, $\sum\Delta d/\sum w_2 = 0{\cdot}1875$, $\sum\Delta n/\sum w_2 = 0{\cdot}199$, and $10^7\sum\Delta B/\sum w_2 = 5{\cdot}50$.

Solute: *Dibenzylideneacetone.*

$10^6 w_2$	4484	8690	13,080	17,613	23,116	27,023
ε_{12}	2·2980	2·3229	2·3467	2·3720	2·4044	2·4262
d_{12}	0·87460	0·87546	0·87618	0·87711	0·87815	0·87884
$10^4 \Delta n$	8·5	15	22	27	36	44
$10^6 w_2$	3293	5820	7837	9672		
$10^7 \Delta B$	−0·015	−0·027	−0·037	−0·045		

whence $\sum\Delta\varepsilon/\sum w_2 = 5{\cdot}693$, $\sum\Delta d/\sum w_2 = 0{\cdot}1872$, $\sum\Delta n/\sum w_2 = 0{\cdot}1622$, and $10^7\sum\Delta B/\sum w_2 = -4{\cdot}66$.

Solute: *Dicinnamylideneacetone.*

$10^6 w_2$	2557	5386	10,911	12,998	14,142	18,144	20,500	24,176
ε_{12}	2·2859	2·2997	2·3266	2·3354	2·3432	2·3630	2·3751	2·3938
d_{12}	0·87422	0·87474	0·87569	0·87608	0·87624	0·87711	0·87756	0·87809
$10^4 \Delta n$	7	15	28	35	38	48	55	64
$10^7 \Delta B$	−0·041	−0·064	−0·130	−0·146	−0·167	−0·211	−0·237	−0·280

whence $\sum\Delta\varepsilon/\sum w_2 = 4{\cdot}987$, $\sum\Delta d/\sum w_2 = 0{\cdot}1791$, $\sum\Delta n/\sum w_2 = 0{\cdot}2665$, and $10^7\sum\Delta B/\sum w_2 = -11{\cdot}72_6$.

* $\Delta B = B_{12} - B_1$; $\Delta n = n_{12} - n_1$.

out with nitrogen before and after weighings. To avoid photoisomerisation,[6] all compounds theoretically capable of geometrical change, either as pure solutes or as solutions, were kept in the dark and examined in as weak a light as possible.

Apparatus, Procedures, and Methods of Calculation.—These have been fully described before.[7-9] Measurements, taken in all cases at 25°, are listed in Table 1 under the usual heading. Various quantities deduced from Table 1, leading to dipole moments and molar Kerr constants, are given in Table 2. Formulæ and symbols used here are, for molar Kerr constants, as defined on p. 283 of the review article,[7] for total polarisations, as on p. 56 of ref. 8. Concentrations are expressed as weight fractions, w_2. When $w_2 = 0$, $\varepsilon_1 = 2{\cdot}2725$, $d_1 = 0{\cdot}87378$, $n_1 = 1{\cdot}4973$ (Na_D light), $B_1 = 0{\cdot}410 \times 10^{-7}$, $p_1 = 0{\cdot}34086$, $c = 0{\cdot}18809$, $H = 2{\cdot}114$, $J = 0{\cdot}4681$, and ${}_{s}K_1 = 7{\cdot}56 \times 10^{-14}$.

TABLE 2.

Polarisations, dipole moments, molar Kerr constants, etc., at infinite dilution in benzene at 25°.

Solute	$\alpha\varepsilon_1$	β	γ	δ	${}_{\infty}P_2$ (c.c.)	$[R_L]_D$ (c.c.)	μ(D)	${}_{\infty}({}_{m}K_2) \times 10^{12}$
Benzaldehyde	$9{\cdot}06_8$	0·1667	0·028	54·32	211·1	32·1	2·96	408
Cinnamaldehyde	10·93	$0{\cdot}177_6$	0·068	154·2	308·7	44·3	3·59	1497
11-Phenylhendecapentaenal	10·45	$0{\cdot}189_7$	(0·554) *	1169·0	529·6	(176)	(4·16)	20,795
Benzophenone	$5{\cdot}67_6$	$0{\cdot}226_7$	0·061	$3{\cdot}62_4$	242·6	57·0	3·01	23·0
Benzylideneacetophenone	$5{\cdot}28_9$	$0{\cdot}221_3$	0·101	4·80	262·4	72·2	3·05	48·1
Cinnamylideneacetophenone	$4{\cdot}90_6$	$0{\cdot}214_6$	0·133	$13{\cdot}4_1$	278·9	88·3	3·05	208
Dibenzylideneacetone	$5{\cdot}69_3$	$0{\cdot}214_2$	0·108	$-11{\cdot}36_6$	313·6	83·4	3·36	−238
Dicinnamylideneacetone	$4{\cdot}98_7$	0·2050	0·178	−28·60	346·4	119·9	3·33	−657

* Through sparing solubility values of Δn were very uncertain. Reasons are given later for thinking that $[R_L]_D$ might be about 124 c.c., in which case $\mu = 4{\cdot}4$ D.

Previous Determinations.—For the conditions used here, dipole moments (D) have been reported as follows: benzaldehyde 2·75 (ref. 10), 2·77 (ref. 11), 2·98 (ref. 12); cinnamaldehyde 3·71 (ref. 13), 3·63 (ref. 14); benzophenone 2·95 ± 0·03 (ref. 15), 2·95 (ref. 16), 3·00 ± 0·02 (ref. 17), 2·95 (ref. 18), 2·99 (ref. 16); benzylideneacetophenone 2·98—3·02 (ref. 20), 3·01 (ref 21), 2·92 (ref. 22); dibenzylideneacetone 3·28 (ref. 13).

No molar Kerr constants for any of these solutes are on record; a solitary datum having a slight relevance is that the electric birefringence of liquid benzaldehyde relatively to carbon disulphide is 24·96 at 15·2° (I.C.T., Vol. VII, p. 109).

DISCUSSION

Exaltations of Polarisability.—These are first estimated directly as $\Delta b = A - B$, where $A = 10^{-23}(b_1 + b_2 + b_3) = 9({}_{E}P)/4\pi N = 0{\cdot}11891 \times 10^{-23}({}_{E}P)$, ${}_{E}P$ being taken as $0{\cdot}95R_D$, and B is obtained by summing the longitudinal, transverse, and " vertical " polarisabilities (b_L, b_T, and b_V, respectively) of the various bonds concerned. The values used are those

[6] Wyman, *Chem. Rev.*, 1955, **55**, 625.
[7] Le Fèvre and Le Fèvre, *J.*, 1953, 4041; 1954, 1577; *Rev. Pure Appl. Chem.*, 1955, **5**, 261.
[8] Le Fèvre, " Dipole Moments," Methuen, London, 3rd edn., 1953, Chap. 2.
[9] Buckingham, Chau, Freeman, Le Fèvre, Rao, and Tardif, *J.*, 1956, 1405.
[10] Williams, *J. Amer. Chem. Soc.*, 1928, **50**, 2350.
[11] Goebel and Wenzke, *J. Amer. Chem. Soc.*, 1937, **59**, 2301.
[12] Calderbank and Le Fèvre, *J.*, 1949, 1462.
[13] Hassel and Naeshagen, *Z. phys. Chem.*, 1930, *B*, **6**, 441.
[14] Bentley, Everard, Marsden, and Sutton, *J.*, 1949, 2957.
[15] Wolf, *Phys. Z.*, 1930, **31**, 227.
[16] Bergmann, Engel, and Meyer, *Ber.*, 1932, **65**, 446.
[17] Fuchs and Donle, *Z. phys. Chem.*, 1933, *B*, **22**, 1.
[18] Granier, *Compt. rend.*, 1946, **223**, 893.
[19] Müller, *Phys. Z.*, 1933, **34**, 689.
[20] Eisenlohr and Metzner, *Z. phys. Chem.*, 1937, *A*, **178**, 350.
[21] Le Fèvre, *J.*, 1937, 1037.
[22] Bergmann, *J.*, 1936, 402.

secured by previous work [1,2,7,23] on " isolated " bonds; for the phenyl group the polarisabilities are those of benzene less the (isotropic) polarisability of one C–H link:

	C–H	C–C	C=C	C=O	Ph
$10^{23}b_L$	0·064	0·099	0·280	0·230	1·056
$10^{23}b_T$	0·064	0·027	0·073	0·140	1·056
$10^{23}b_V$	0·064	0·027	0·077	0·046	0·672

In conjunction with the R_D's of Table 2 we accordingly find Δb's as in Table 3.

TABLE 3.

Estimates of exaltations of polarisability from refractivity and bond data.

	$10^{23}A$	$10^{23}B$	$10^{23}(A - B) = 10^{23}\Delta b$
Benzaldehyde	3·63	3·55	0·08
Cinnamaldehyde	5·00	4·51	0·49
Benzophenone	6·44	6·29	0·15
Benzylideneacetophenone	8·16	7·26	0·90
Cinnamylideneacetophenone	9·98	8·22	1·76
Dibenzylideneacetone	9·42	8·22	1·20
Dicinnamylideneacetone	13·54	10·16	3·38

Bramley and Le Fèvre [2] noted that the exaltations of polarisability in the $\alpha\omega$-diphenylpolyenes could be correlated with the wavelengths of maximum absorption of their respective K-bands by equations of the type: $\Delta b = C(\lambda - D)^3$. For the seven molecules under consideration, values of $C = 6{\cdot}165 \times 10^{-7}$ and $D = 197$ give (by insertion of λ as mμ) the results in Table 4; Δb's calculated in this way are sensitively dependent on $\lambda_{max.}$; *e.g.*, were $\lambda_{max.}$ in the last two cases 322 and 373 mμ, instead of 330 and 375 mμ, respectively, the calculated and the found Δb's would be identical; since such variations in $\lambda_{max.}$ can be due to solvent effects (cf. ref. 24, pp. 115, 265) it is mentioned that the wavelengths used in Table 4 are all those observed for alcoholic solutions.

TABLE 4.

Calculation of exaltations of polarisability as $\Delta b = 6{\cdot}165 \times 10^{-7}(\lambda_{max.} - 197).^3$

	$\lambda^K_{max.}$ (mμ)	$10^{23}\Delta b$ (calc.)	$10^{23}\Delta b$ (found)
Benzaldehyde	244 [a]	0·06$_4$	0·08
Cinnamaldehyde	289 [a]	0·48	0·49
Benzophenone	252 [b]	0·10	0·15
Benzylideneacetophenone	310 [b]	0·89	0·90
Cinnamylideneacetophenone	342 [c]	1·88	1·76
Dibenzylideneacetone	330 [b]	1·45	1·20
Dicinnamylideneacetone	375 [b]	3·48	3·38

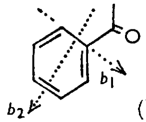
[a] Ref. 24, p. 126. [b] Ref. 25, p. 126. [c] Ref. 26.

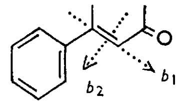
Under " Solutes," and below Table 2, we have drawn attention to practical difficulties with 11-phenylhendecapentaenal. Krauss and Grund [27] record $\lambda_{max.}$ for the K band of this molecule as 407 mμ; Δb calc. is therefore $5{\cdot}71 \times 10^{-23}$. Summing the b_L's, b_T's, and b_V's of the component bonds (as though they were " isolated " bonds) gives $8{\cdot}38 \times 10^{-23}$; $b_1 + b_2 + b_3$ for the real structure then follows as $14{\cdot}09 \times 10^{-23}$, whence $_EP = 118{\cdot}5$, and $_DP = ca.\ 1{\cdot}1(_EP) = 130{\cdot}3$ c.c. From Table 2, $_\infty P_2$ is 529·6 c.c., so that μ should be 4·4$_2$ D.

Conformations and Anisotropies of Polarisability of the Solutes.—For benzaldehyde and cinnamaldehyde we assume that the exaltation of polarisability acts entirely along the direction of $\mu_{C=O}$ and that all CCC and CCO angles are 120°; in both structures the benzene

[23] Le Fèvre, Le Fèvre, and Rao, *J.*, 1959, 2340.
[24] Gillam and Stern, " An Introduction to Electronic Absorption Spectroscopy in Organic Chemistry," Arnold, London, 1954.
[25] Braude, *Ann. Reports*, 1945, **42**, 126.
[26] Thomas and Branch, *J. Amer. Chem. Soc.*, 1953, **75**, 4793.
[27] Krauss and Grund, *Z. Elektrochem.*, 1954, **58**, 767.

rings may or may not be coplanar with the atoms to which they are attached, and in cinnamaldehyde there are theoretically possibilities of *cis-trans*-forms and rotations of


(I)


(II)

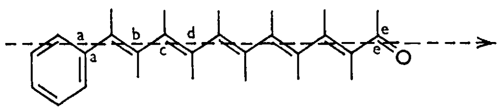
the aldehyde group as well. Since resonance favours flatness we start with the planar models (I) and (II). When the bond and " phenyl " polarisabilities already listed are used, the computed principal axes and corresponding ${}_{m}K$'s calc. are:

	$10^{23}b_1$	$10^{23}b_2$	$10^{23}b_3$	$10^{12}{}_{m}K$ (calc.)	$10^{12}{}_{m}K$ (obs.)
For (I)	1·396	1·341	0·809	326	408
For (II)	1·848	1·623	1·041	760	1497

The obvious deficiencies in the calculated ${}_{m}K$'s become worse if non-planar variants of forms (I) and (II) are examined. Addition of the exaltation (Table 4) to b_1 improves the situation (headings as before):

For (I)	1·476	1·341	0·809	407	408
For (II)	2·338	1·623	1·041	1495	1497

The agreement between ${}_{m}K$ (calc.) and ${}_{m}K$ (obs.) for both these aldehydes is excellent and suggests that the relative dispositions of $b_{max.}$ and $\mu_{resultant}$ are approximately correct, although mesomeric shifts and mesomeric moments should cause $b_{max.}$ and $\mu_{resultant}$ to lie somewhat anticlockwise to the C=O axes of forms (I) and (II). Such effects of mesomerism must be pronounced in the highly conjugated 11-phenylhendecapentaenal (III), which we assume to be a flat molecule in which the all-*trans*-zig-zag polyene chain has CCC angles of 124·4° [the mean of 123·9°, 124·8°, and 124·5°, *i.e.*, of those corresponding in crystalline diphenyloctatetrene [28] to b, c, and d in (III)]; the angles at a we take as 120°, and that at e as 123°. For reasons explained by Bramley and Le Fèvre [2] the " bisector axis " (the line joining the mid-points of the bonds in the polyene chain) is used as the principal direction of greatest polarisability. The resultant dipole moment, 4·42 D, compounded


(III)

of $\mu_{mesomeric}$ plus $\mu_{C=O}$, probably acts *ca.* 20° from $b_{max.} = b_1$, but even if it be assumed to act parallel to b_1 (in order to obtain a maximum estimate of ${}_{m}K$) the ${}_{m}K$ (calc.) is far too low:

For (III)	3·628	2·783	1·969	2805	20,800

By the equation used in Table 4, with [27] $\lambda = 407$ mμ, Δb appears as $5·71 \times 10^{-23}$; this, added to b_1, produces an ${}_{m}K$ nearer that found:

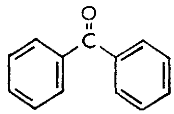
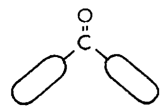
For (III)	9·34	2·78	1·97	17,500	20,800

Any conformation other than " all *s-trans* " increases the disagreement between the calculated and the found ${}_{m}K$.

Inspection of Courtauld models of benzophenone shows that steric hindrance to a flat structure is considerable, and suggests that the benzene rings are each out of plane by *ca.* 40°. Jones [29] in 1945 had suggested, from ultraviolet spectral evidence, that the interplanar angle was 30°. Hampson and Sutton,[30] and Bergmann, Engel, and Meyer [30]

[28] " Tables of Interatomic Distances and Configuration in Molecules and Ions," Ed. Sutton, *Chem. Soc. Spec. Publ.* No. 11, 1958, M 249.
[29] Jones, *J. Amer. Chem. Soc.*, 1945, **67**, 2127.
[30] Bergmann, Engel, and Meyer, *Ber.*, 1932, **65**, 446; Hampson and Sutton, *Trans. Faraday Soc.*, 1935, **31**, 945.

found, by dipole moment measurements, that 131° is a reasonable estimate of the Ph–C–Ph angle. We here calculate the polarisabilities and molar Kerr constants expected for the structures (IVa and b) (in which the phenyl groups are, respectively, coplanar with, and perpendicular to, the plane containing the C–CO–C unit) and for (IVc) (in which each phenyl group is twisted 45° from coplanarity). Results are as follows (headings as before):

(IVa)   (IVb)

For (IVa)	2·421	2·425	1·444	+535	
For (IVb)	1·785	2·212	2·293	−457	+23
For (IVc)	2·103	2·359	1·828	+20	

The intermediate configuration is thus about correct. No allowance has been made for the small exaltation of $0{\cdot}15 \times 10^{-23}$ c.c. (cf. Table 4), nor is it clear how to make this; if Δb_1 is 0·05 and Δb_2 is 0·10, then for (IVc) the calculated ${}_{\mathrm{m}}K$ is $+24 \times 10^{-12}$; if the exaltation is wholly added to b_2, then ${}_{\mathrm{m}}K$ (calc.) is -48×10^{-12}. These calculations are sensitively affected by the angles of twist taken for the phenyl groups; *e.g.*, for a 40° twist (IVc′) or a 41° twist (IVc″), instead of 45°, we have:

For (IVc′)	2·158	2·409	1·723	+110	+23
For (IVc″)	2·147	2·408	1·735	+93	

and with the exaltation added to b_2 these become:

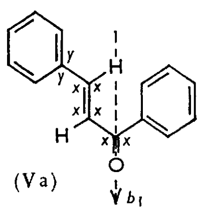
For (IVc′)	2·158	2·559	1·723	+43	+23
For (IVc″)	2·147	2·558	1·735	+26	

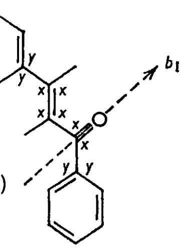
For benzylideneacetophenone there are the *s-trans-* and the *s-cis*-planar alternatives (Va and b), in which the angles marked x and y are assumed to be 123° and 120°, respectively (123° is the angle adopted by Bentley *et al.*[14] for the conjugated ketones discussed by them). With headings as before we have:

For (Va)	2·895	2·686	1·676	797	48·1
For (Vb)	2·722	2·859	1·676	530	

If the exaltation of polarisability ($0{\cdot}9 \times 10^{-23}$ c.c.) occurs along the b_{maximum} axis, ${}_{\mathrm{m}}K$ (calc.) for form (Va) becomes larger still; that for form (Vb) becomes:

For (Vb)	2·722	3·759	1·676	167	48·1


(Va)


(Vb)

The positivities of the ${}_{\mathrm{m}}K$'s calculated without addition of exaltation for (Va and b) are reduced if the benzene rings are twisted out of the plane of the C=C–C=O unit; when they are perpendicular we have:

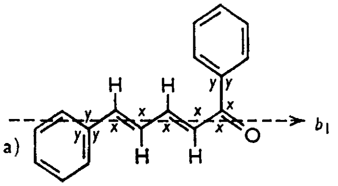
For (Va)	2·355	2·458	2·444	−99	48·1
For (Vb)	2·182	2·631	2·444	−358	

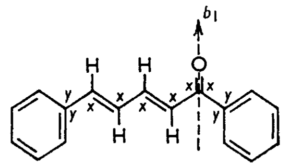
Thus for benzylideneacetophenone a non-planar variation is indicated of the conformation for which ${}_{\mathrm{m}}K$ (calc.) above was 167×10^{-12}; if the two benzene rings are twisted 20° around their 4,1-axes, the last line of data would read:

For (Vb) (20°)	2·659	3·732	1·766	52·8	48·1

For cinnamylideneacetophenone we initially considered the *s-trans,s-cis*-form (VIb) [the angles x and y are as in (Va and b)] but when account is taken of the exaltation ($1{\cdot}76 \times 10^{-23}$ c.c.) the least negative ${}_{\mathrm{m}}K$ which could be expected was -110×10^{-12}:

For (VIb)	3·006	5·070	1·908	−110	+208

(VIa) 

 (VIb)

The *s-trans,s-trans*-alternative (VIa), with the exaltation acting along the bisector axis, corresponds to a very large positive molar Kerr constant:

For (VIa)	5·057	3·019	1·908	+2115	+208

Calculations can only be reconciled with experiment if the true conformation is intermediate between (VIa) and (VIb), or if the substance examined is a mixture of *ca.* 86% of (VIb) with 14% of (VIa).

The *s-trans,s-trans*-form of dibenzylideneacetone requires a positive Kerr constant greatly exceeding the negative value observed. The *s-cis,s-cis*-isomer (VII), with an exaltation of $1{\cdot}20 \times 10^{-23}$ c.c. added to b_2, leads to the following:

For (VII)	3·006	4·510	1·908	+2·7	−238

If the benzene rings in form (VII) are twisted out of plane by the angles in parentheses, these quantities become:

For (VII) (25°)	2·910	4·467	2·047	−207	−238
For (VII) (28°)	2·887	4·460	2·077	−256	

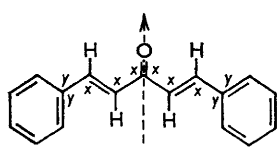
Calculated and observed molar Kerr constants agree for angles between 26° and 27°.

A similar treatment can be given to dicinnamylideneacetone, shown as the *s-trans,s-cis,s-cis,s-trans*-planar conformation in (VIII); the all-*trans*-variety need not be considered since it requires an extremely large positive ${}_{\mathrm{m}}K$, in contrast to that observed, which is large and negative. Addition of the exaltation ($3{\cdot}38 \times 10^{-23}$ c.c.) to b_2 gives:

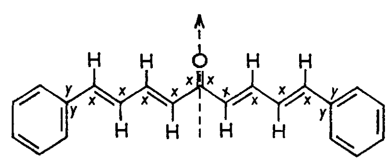
For (VIII)	3·766	7·400	2·372	−361	−657

Twisting the terminal benzene-rings about their 1,4-lines by the amounts shown in parentheses modifies these predictions as follows:

For (VIII) (10°)	3·750	7·393	2·395	−399	
For (VIII) (20°)	3·703	7·373	2·462	−510	−657
For (VIII) (30°)	3·631	7·343	2·564	−676	



(VII)



(VIII)

In the last instance an angle of 29° would produce the observed molar Kerr constant. However, owing to the various assumptions made, errors of measurement, etc., such precise quantitative deductions are unjustified; moreover, some rotations possibly occur around bonds other than those between phenyl and carbon (cf. cinnamylideneacetophenone above). That the benzene rings in the unit Ph·CH=CH will tend to be forced out of the C_{Ar}–C=C plane by steric causes is understandable from the scale drawing reproduced in ref. 14 as Fig. 2—the van der Waals' radii of an *ortho*-H and the next but one of the C–H links overlap. The literature does not offer much with which to compare present conclusions, although we note that, in situation at least, there is some analogy between the phenyl groups in phenylenes and those in the Ph·C=C portions of our molecules, consistently with twisting of the phenyl groups in 1,3,5-triphenylbenzene out of the central plane by $+34°$, $-27°$, and $+24°$, *i.e.*, by angles resembling in magnitude those needed here with benzylideneacetophenone and dibenzylidene- and dicinnamylidene-acetone. Bentley *et al.*[14] argued from resultant dipole moments that cinnamaldehyde was *s-trans*, and that dibenzylideneacetone was most probably *s-cis,s-cis*; our results above agree qualitatively with such assignments.

The measurements of ΔB *versus* w_2 for benzylideneacetophenone and cinnamylideneacetophenone, and a confirmatory run for the sparingly soluble phenylhendecapentaenal, were made by Dr. M. Aroney whose assistance is gratefully acknowledged.

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