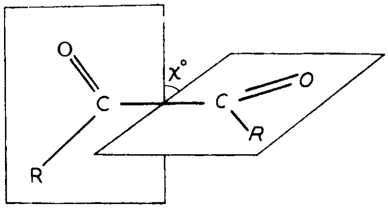
876. *Molecular Polarisability: the Conformations of Biacetyl, Benzil, and Furil as Solutes in Benzene or Carbon Tetrachloride.*

By (Miss) P. H. Cureton, (Mrs.) C. G. Le Fèvre, and R. J. W. Le Fèvre.

Measurements of dipole moments, refractivities, molar Kerr constants, etc., of the molecules named in the title, and of phenanthraquinone and furfuraldehyde, indicate that the effective (or average) conformations of biacetyl, benzil, and furil are non-planar (as in I) with azimuthal angles χ^0 *ca.* 160°, 97°, and 118·5° respectively. The phenyl or furyl groups may be twisted about the Ph–(CO) or (C_4H_3O)–(CO) bonds by 5° in the former, or 1° in the latter, case. Data for furfuraldehyde are consistent with the *s-trans*-conformation (II).

In 1939 Caldwell and Le Fèvre [1] suggested that " the stable configuration of benzil in non-polar solvents is one in which the ketonic groups, with their appropriate bonds, are effectively situated in, or make rotational oscillations of low amplitude about, two planes which are roughly mutually perpendicular " (see I). Their evidence was drawn from dipole-moment measurements plus the fact that benzil showed a strong negative Kerr effect in contrast to the small or large positive effects expected respectively for the planar *cis*- or *trans*-variant of (I). Only the molar Kerr constants of benzene and phenanthraquinone have so far been published; [2] this paper now presents the missing observational details and extends the inquiry to biacetyl and furil.



(I)

Experimental

Solutes.—Benzil and furil, prepared from benzaldehyde or furfuraldehyde by standard methods,[3] had m. p. 94—95° and 165—166° (from carbon tetrachloride or methanol respectively). Biacetyl (from L. Light) was dried ($CaCl_2$, then $MgSO_4$) before distillation at 20 mm.; a small quantity, purified through the orthophosphoric acid complex,[4] gave the same dielectric constant increments in both benzene and carbon tetrachloride as the main material. Phenanthraquinone, recrystallised from ethanol, had m. p. 205°. Furfuraldehyde, when required for measurements, was dried ($MgSO_4$) and redistilled immediately before the solutions were made up.

Solvents, Apparatus, and Methods.—Benzene and carbon tetrachloride were as specified in ref. 5, p. 45. Dielectric constants have been determined with the apparatus described in ref. 6, electric double refractions by that in ref. 2, pp. 274—280, or ref. 7, pp. 2462—2481. Procedures for calculating total polarisations at infinite dilution, $_\infty P_2$, and molar Kerr constants at infinite dilution, $_\infty(_mK_2)$, from measurements of the dielectric constants, ε_{12}, densities, d_{12}, refractive indexes, n_{12}, and Kerr constants B_{12}, for a solution containing a weight fraction w_2 of solute, are explained in refs. 2, 5, and 7, wherein also other symbols used here are defined. (Subscript 1 indicates solvent, 2 indicates solute, and 12 indicates solution.)

Measurements and Results.—The differences observed between solution and solvent for the various properties are recorded in Table 1, where, *e.g.*, $\Delta\varepsilon$ signifies $\varepsilon_{12} - \varepsilon_1$, ΔB signifies B_{12} —

---

[1] Caldwell and Le Fèvre, *J.*, 1939, 1614.
[2] Le Fèvre and Le Fèvre, *Rev. Pure Appl. Chem.*, 1955, **5**, 261.
[3] Vogel, " A Text-Book of Practical Organic Chemistry," Longmans Green and Co., London, 1948, pp. 678—679, 795.
[4] Olivier, *Bull. Soc. chim. France*, 1932, **51**, 99.
[5] Le Fèvre, " Dipole Moments," Methuen, London, 3rd edn., 1953.
[6] Buckingham, Chau, Freeman, Le Fèvre, Rao, and Tardif, *J.*, 1956, 1405.
[7] Le Fèvre and Le Fèvre, in " Physical Methods of Organic Chemistry," Part 3 of " Technique of Organic Chemistry," ed. A. Weissberger, Interscience Publ., Inc., New York, 3rd edn., 1960.

TABLE 1. *Increments of dielectric constant, density, Kerr constant, etc., of solvents due to concentrations* w_2 *of solute.*

Biacetyl in carbon tetrachloride at 25°

$10^6 w_2$	1943	8681	10,192	13,257	18,262	22,683	28,610	38,826
$10^4 \Delta\varepsilon$	58	179	201	267	319	445	525	758
$-10^5 \Delta d$	224	922	—	1410	1947	—	3046	—
$-10^4 \Delta n$	6	16	—	21	26	—	38	53
$10^6 w_2$	6265	8085	12,030	13,845	17,302	19,199		
$-10^{10} \Delta B$ ...	11	13	23	26	32	35		

whence $\sum\Delta\varepsilon/\sum w_2 = 1{\cdot}932$; $\sum\Delta d/\sum w_2 = -1{\cdot}067$; $\sum\Delta n/\sum w_2 = -0{\cdot}146_0$; $\sum\Delta B/\sum w_2 = -1{\cdot}82_5 \times 10^{-7}$; and $\sum(n_{12}^2 - n_1^2)/\sum w_2 = -0{\cdot}430$.

Biacetyl in benzene at 25°

$10^6 w_2$	5090	5271	6434	9844	10,480	15,336	21,495	21,730	27,362	29,680
$10^4 \Delta\varepsilon$	65	—	—	110	—	169	252	—	316	—
$10^5 \Delta d$	—	33	46	—	69	—	—	140	—	207
$10^6 w_2$	10,776	21,086	29,037	40,165						
$-10^4 \Delta n$	15	25	33	49						
$10^6 w_2$	15,336	21,113	21,495	27,362	29,434	33,998	41,691			
$-10^{10} \Delta B$ ...	33	36	40	51	57	68	78			

whence $\sum\Delta\varepsilon/\sum w_2 = 1{\cdot}153$; $\sum\Delta d/\sum w_2 = 0{\cdot}0673$; $\sum\Delta n/\sum w_1 = -0{\cdot}120_7$; $\sum\Delta B/\sum w_2 = -1{\cdot}90_6 \times 10^{-7}$; and $\sum(n_{12}^2 - n_1^2)/\sum w_2 = -0{\cdot}3557$.

Benzil in carbon tetrachloride at 20°

$10^5 w_2$	175	671	1063	1174	2023	2496
$-10^{10} \Delta B$ ...	71	216	292	348	554	720

whence $10^7 \Delta B = -29{\cdot}5 w_2 + 0{\cdot}05 w_2^2$.

Benzil in benzene at 25°

$10^5 w_2$	699	2061	2370	2795	2981	3638
$-10^{10} \Delta B$ ...	119	316	367	416	449	646

whence $\sum\Delta B/\sum w_2 = -15{\cdot}9_0$.

Phenanthraquinone in benzene at 20°

$10^5 w_2$	31	34	76	112	149
$10^{10} \Delta B$ ...	21·5	27	56	78	105

whence $\sum(w_2 \,.\, \Delta B)/\sum w_2^2 = 70{\cdot}9 \times 10^{-7}$.

Furil in benzene at 25°

$10^6 w_2$	1481	1741	3550	3843	4477	4599	5715	7346	8526	8782
$10^4 \Delta\varepsilon$	101	105	211	218	287	276	346	448	511	546
$10^6 w_2$	1978	3087	3373	4395	6634					
$10^5 \Delta d$ ...	56	92	101	130	192					
$10^6 w_2$	1344	2552	4201	4914	5248	5269	6563	7096	7819	
$-10^{10} \Delta B$ ...	21	43	66	89	91	94	104	117	137	
$10^6 w_2$	4049	5402	7197	7884						
$10^4 \Delta n$ ...	3	4	5	6						

whence $\sum\Delta\varepsilon/\sum w_2 = 6{\cdot}091$; $\sum\Delta d/\sum w_2 = 0{\cdot}2933$; $\sum\Delta B/\sum w_2 = -16{\cdot}93 \times 10^{-7}$; $\sum\Delta n/\sum w_2 = 0{\cdot}073_4$, and $\sum(n_{12}^2 - n_1^2)/\sum w_2 = 0{\cdot}2160$.

Furfuraldehyde in carbon tetrachloride at 25°

$10^6 w_2$	4045	4672	13,019	31,026
$10^4 \Delta\varepsilon$	983	1148	3236	8016
$10^4 \Delta n$ ...	3	4	9	26
$10^6 w_2$	9818	2015	2385	3207
$-10^5 \Delta d$	612	1222	1563	1958

whence $\sum\Delta\varepsilon/\sum w_2 = 25{\cdot}36_5$; $\sum\Delta d/\sum w_2 = -0{\cdot}623_5$; $\sum(n_{12}^1 - n_1^2)/\sum w_2 = 0{\cdot}2331$.

Furfuraldehyde in benzene at 25°

$10^6 w_2$	2685	4666	5290	6615	9245	10,549
$10^{10} \Delta B$ ...	102	186	216	292	368	439

whence $\sum\Delta B/\sum w_2 = 41{\cdot}05 \times 10^{-7}$.

B_1, etc. When $w_2 = 0$, we have, for ε_1, d_1, $(n_D)_1$, B_1, etc., and the various constants which enter calculations leading to Table 2, the following:

	ε_1	d_1	$(n_D)_1$	B_1	p_1 (c.c.)	C	H	J	$10^{14}{}_sK_1$
Benzene 20°	2·2825	0·8791	1·5010	0·424	—	—	2·119	0·4670	7·72
,, 25°	2·2725	0·8738	1·4973	0·410	0·34086	0·18809	2·114	0·4681	7·56
CCl_4 20°	2·2360	1·5940	1·4604	0·072	—	—	2·064	0·4721	0·761
,, 25°	2·2270	1·5845	1·4574	0·070	0·18319	0·10596	2·060	0·4731	0·749

DISCUSSION

Dipole Moment of Biacetyl.—The present measurements on biacetyl are reconcilable with those made on the vapour by Bloom and Sutton [8] which showed the resultant moment to rise from 1·05 D at 55° to 1·27 D at 205°. Zahn [9] had previously also reported an increase, 1·25 to 1·48 D, over the temperature range 66° to 231°. Biacetyl has here been examined in two solvents (carbon tetrachloride and benzene) because of the high polarity (1·8 D) earlier claimed in benzene by Caldwell and Le Fèvre; [1] since in all details the data in ref. 1 for biacetyl differ from those in Table 1 of this paper, we conclude that Caldwell and Le Fèvre were not working with the pure diketone, and their value should be replaced accordingly. Bloom and Sutton [8] computed the apparent orientation polarisations at five temperatures on the assumption that the distortion polarisation was 22·7 c.c.; the apparent moments so obtained give smooth plots against temperature and suggest, by extrapolation, that μ at 298° K, corresponding to our measurements, might be 0·8—0·9 D. Since an unknown fraction of the total polarisation may be "vibration polarisation," the values of μ given by Bloom and Sutton and in Table 2 must be regarded as upper estimates.

TABLE 2. *Calculations of polarisations, moments, and molar Kerr constants from Table* 1.

Solute	Sol-vent	$\alpha\varepsilon_1$	β	γ	δ	$_\infty P_2$ (c.c.)	R_D (c.c.)	μ (D)	$10^{12}{}_\infty({}_mK_2)$
Biacetyl	CCl_4	1·932	−0·673	−0·100	−26·0$_7$	44·0	20·7	1·0$_4$	−16·3
,, ...	C_6H_6	1·153	0·0770	−0·08$_1$	−4·64$_9$	45·8	20·8	1·0$_8$	−27·2
Benzil	CCl_4	12·58 [a]	−0·341 [a]	0·394 [a]	−410	—	—	3·60 [a]	−663
,, ...	C_6H_6	7·66 [a]	0·260 [a]	0·060 [a]	−38·7$_9$	—	—	3·76 [a]	−663
Phenanthraquinone	C_6H_6	16·81$_5$ [a]	0·347 [a]	0·092 [a]	167·2	—	—	5·57 [a]	2570
Furil	C_6H_6	6·091	0·336	0·049	−41·30	260·9	50·2	3·19	−626
Furfuraldehyde ...	CCl_4	25·36$_5$	−0·393$_5$	—	—	282·8	25·5	3·5$_4$	—
,, ...	C_6H_6	15·2 [b]	0·332 [b]	0·047	100·1	—	—	3·6$_3$ [b]	680

[a] From Caldwell and Le Fèvre.[1] [b] From Calderbank and Le Fèvre (*J.*, 1949, 1462).

TABLE 3. *Molecular and bond polarisabilities.**

	Benzene	Furan	C–H	C–C	C=O
b_1 (or b_L)	1·12$_0$	0·743	0·064	0·099	0·230
b_2 (or b_T)	1·12$_0$	0·889	0·064	0·027	0·140
b_3 (or b_V)	0·73$_6$	0·537	0·064	0·027	0·046
Source ref.	[a]	[b]	2	2	[c]

* Quoted here, and throughout this paper, in units of 10^{-23} c.c.

[a] Aroney and Le Fèvre, *J.*, 1960, 3600. [b] Le Fèvre, Le Fèvre, Rao, and Smith, *J.*, 1959, 1188. Le Fèvre, Le Fèvre, and Rao, *J.*, 1959, 2340.

Anisotropic Molecular and Bond Polarisabilities used.—Table 3 lists the principal polarisabilities (b_1, b_2, and b_3) of benzene and furan, and the longitudinal, transverse, and "vertical" polarisabilities (b_L^{XY}, b_T^{XY}, and b_V^{XY}) of bonds X–Y required for the calculations which follow.

The general approach has been to estimate the azimuthal angle χ from dipole-moment considerations, then to apply relevant information from Table 3 to the indicated appropriate molecular geometry, thus obtaining b_1, b_2, and b_3 for the solute species (b_1 is consistently

---

[8] Bloom and Sutton, *J.*, 1941, 727.

[9] Zahn, *Phys. Rev.*, 1932, **40**, 291.

measured along the direction of action of $\mu_{\text{resultant}}$), and finally to compute the molar Kerr constant ${}_{\text{m}}K$ expected for the specified conformation, and to compare ${}_{\text{m}}K$ calc. with ${}_{\text{m}}K$ found.

The Conformation of Biacetyl.—Lu Valle and Schomaker[10] reported that electron-diffraction experiments indicated that biacetyl is coplanar, with a *trans*-configuration, although the possibility that it is a mixture containing a small fraction of *cis*-molecules was not excluded. Bloom and Sutton,[8] discussing the temperature dependence of μ_{diacetyl}, leave undecided whether " there be an equilibrium between *cis*- and *trans*-forms or an unusually rigid fixation in the *trans*-configuration," although they " conclude that there is a very strong tendency for the molecule to be planar." Mizushima[11] asserts that crystals of biacetyl contain only the *trans*-configuration.

The fact (Table 2) that, as a solute, biacetyl shows a *negative* molar Kerr constant is qualitatively incompatible with a mixture of planar *cis*- and *trans*-isomers, since each of these should have a *positive* ${}_{\text{m}}K$ (see Table 4). Further, scale drawings involving the bond lengths and angles given by Lu Valle and Schomaker, plus the " Wirkungsradien " of Stuart[12] (which are *less* than those proposed by Pauling[13]), reveal mutual penetrations of *ca.* 0·4 Å by the spheres of the methyl group and the carbonyl-oxygen atom in the flat *trans*-arrangement, and of *ca.* 1·2 Å by the two methyl groups in the *cis*-arrangement. A skew structure is therefore likely to be more stable than either planar form.

The resultant dipole moment of a 1,2-diketone such as (I), with C–C–O and C–C–C angles of 120°, is:

$$\mu_{\text{r}} = \mu_{\text{CO}}\cos 30° \, [2(1 + \cos\chi)]^{0{\cdot}5}$$

An estimate of the μ_{CO} component can be made from the moment of camphorquinone (4·46 D; Le Fèvre, Maramba, and Werner[14]), a molecule in which the carbonyl groups are fixed by attachment in a rigid cage of C–C links. If all angles are accepted as tetrahedral, the two μ_{CO} vectors interact at 70°, so that $\mu_{\text{CO}} = 2{\cdot}72$ D. This datum, with $\mu_{\text{diacetyl}} = 1{\cdot}08$ D, yields $\chi = 153{\cdot}5°$; polarisabilities, and hence the ${}_{\text{m}}K$ calc., follow as in Table 4. The predicted ${}_{\text{m}}K$ is somewhat too negative; the best compromise, if both μ_{r} calc. and ${}_{\text{m}}K$ calc. are considered, is a conformation with $\chi =$ *ca.* 160°. Since, near $\chi = 160°$, the rates of change of μ_{r} and ${}_{\text{m}}K$ with χ are linear and non-linear respectively, the greater differences (Table 2) between the ${}_{\text{m}}K$s than between the apparent moments in benzene and carbon tetrachloride could be partly due to biacetyl's having a greater amplitude of vibration in

TABLE 4. *Polarisabilities,* dipole moments, and ${}_{\text{m}}K$'s expected for biacetyl with various values of the azimuthal angle.*

χ	μ_{r} (calc.)	b_1	b_2	b_3	$10^{12}\,{}_{\text{m}}K$ (calc.)
180°	0	0·530	0·898	1·014	+9·59
160	$0{\cdot}82_1$	0·569	,,	0·975	−20·4
153·5	1·08	0·579	,,	0·965	−39·0
140	1·62	0·607	,,	0·937	−84·9
120	2·36	0·664	,,	0·880	−136·6
100	3·04	0·734	0·898	0·810	−122·0
0	4·73	1·014	,,	0·530	+749·5

* b_1 is measured parallel to μ_{r} in all cases where μ_{r} is non-zero; the location of b_2 along the central C–C bond is, strictly, valid only when $\chi = 0°$, but errors thus introduced are small: when $\chi = 180°$, b_2 will deviate from the C–C line to the maximum extent; calculation, by the method explained in ref. 7, p. 2486, with $b_{xx} = 0{\cdot}898$, $b_{yy} = 1{\cdot}014$, and $b_{zz} = 0{\cdot}530$, gives the principal polarisabilities as 0·896, 1·016, and 0·530, with the first of these located 7° 24′ from the C–C bond. The argument, that for this non-polar conformation ${}_{\text{m}}K$ will be algebraically positive, is not affected.

---

[10] Lu Valle and Schomaker, *J. Amer. Chem. Soc.*, 1939, **61**, 3520.

[11] Mizushima, " Structure of Molecules and Internal Rotation," Academic Press, Inc., New York, 1954, p. 75.

[12] Stuart, *Z. phys. Chem.*, 1935, *B*, **27**, 350.

[13] Pauling, " The Nature of the Chemical Bond," Cornell Univ. Press, New York, 2nd edn., 1945, p. 189.

[14] Le Fèvre, Maramba, and Werner, *J.*, 1953, 2496.

the former medium than in the latter. Consistently with the suggestion made above, that Sutton's " vibration polarisation " contributes to the measured ${}_{\infty}P_2$, we note that the ${}_{\infty}P_2$ in benzene slightly exceeds that in carbon tetrachloride.

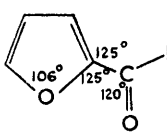
The Conformation of Benzil.—As with biacetyl the negativity of the ${}_{\mathrm{m}}K$ observed eliminates the possibility that benzil as a solute exists as a mixture of planar *cis*- and *trans*-isomers, the ${}_{\mathrm{m}}K$'s of which would be positive; phenanthraquinone can be regarded as a rough substitute for the former conformation. Scale models indicate the likelihood that a skew structure, as proposed in ref. 1, is alone permitted by steric factors. *A priori* calculations of molecular polarisabilities are complicated by ignorance of the degree to which each benzoyl group is itself non-planar.

From $\mu_{\text{phenanthraquinone}} = 5{\cdot}5_7$ D, and from an assumption that C–(CO)–(CO) angles are 120°, μ_{CO} is found to be $3{\cdot}2_3$ D; this, applied to $\mu_{\text{benzil}} = 3{\cdot}7$ D, shows χ to be *ca.* 97°. This value fits the ${}_{\mathrm{m}}K$'s now found, provided (*a*) that the phenyl rings are twisted by 5·1° about their Ph–(CO) bonds from flat arrangements of each Ph·C:O moiety, and (*b*) that all C–C–C angles are 120°:

$$b_1 = 1{\cdot}89_0,\ b_2 = 2{\cdot}62_1,\ b_3 = 2{\cdot}03_5,\ {}_{\mathrm{m}}K \text{ calc.} = -663 \times 10^{-12}$$

On this basis, agreement between prediction and measurement is very satisfactory.

The Conformation of Furil.—The problem here is similar to that with benzil but more complicated because the furyl group, unlike phenyl, contributes a polarity vector to the resultant molecular dipole moment. The moment of furan[15] is 0·72 D, and of furfuraldehyde 3·5—3·6 D; the latter is close enough to the sum of μ_{furan} and[16] $\mu_{\text{benzaldehyde}}$ to justify adopting for furfuraldehyde the *s-trans* conformation (II) in which μ_{r} acts approximately parallel to the C=O axis. If the furoyl radicals in furil resemble (II) and carry moment components of $3{\cdot}6_3$ D, χ for furil ($\mu_{\text{r}} = 3{\cdot}1_9$ D) emerges as 118·5°, and



(II)

$$b_1 = 1{\cdot}38_0,\ b_2 = 2{\cdot}09_1,\ b_3 = 1{\cdot}81_6,\ {}_{\mathrm{m}}K \text{ calc.} = -626 \times 10^{-12}$$

if the planes of the furyl rings are rotated 1° analogously to the rotations described above for the phenyl group in benzil.

The Conformation of Furfuraldehyde.—If for compound (II) angles are adopted as shown (cf. ref. 17 for furan and acraldehyde), together with previously[18] determined polarisabilities of the bonds involved, b_1 (along the C=O bond), b_2 and b_3 can be predicted as 1·18, 0·90, and $0{\cdot}59 \times 10^{-23}$ respectively; these lead to a calculated molar Kerr constant of 623×10^{-12}, a value somewhat less than that observed (680×10^{-12}). From refractivity measurements[19] the electronic polarisation of furfuraldehyde is 24·06 c.c. whence $b_1 + b_2 + b_3 = 2{\cdot}860 \times 10^{-23}$ c.c. compared with the calculated sum of $2{\cdot}67 \times 10^{-23}$ c.c.; evidently there is an exaltation of polarisability of $0{\cdot}19 \times 10^{-23}$ c.c., but the distribution of this cannot be foreseen *a priori*. We note, however, that if this be equally divided between b_1 and b_2 (so that the semi-axes are $1{\cdot}27_5$, $0{\cdot}99_5$, and $0{\cdot}59 \times 10^{-23}$) the calculated ${}_{\mathrm{m}}K$ becomes 686×10^{-12} in good agreement with experiment.

SCHOOL OF CHEMISTRY, THE UNIVERSITY,
SYDNEY, N.S.W., AUSTRALIA.

[*Received, April 4th*, 1961.]

---

[15] Le Fèvre, Le Fèvre, Rao, and Smith, *J.*, 1959, 1188; Harris, Le Fèvre, and Sullivan, *J.*, **1953**, 1622; Buckingham, Harris, and Le Fèvre, *J.*, 1953, 1626.

[16] Calderbank and Le Fèvre, *J.*, 1949, 1462.

[17] *Chem. Soc. Special Publ.*, No. 11, 1958.

[18] Le Fèvre and Le Fèvre, *J.*, 1936, 3549; Bramley, Le Fèvre, Le Fèvre, and Rao, *J.*, 1959, 1183.

[19] Timmermans, " Physico-chemical Constants of Pure Organic Liquids," Elsevier, New York, 1950, p. 501.