67. *Molecular Polarisability. The Molar Kerr Constants, Apparent Dipole Moments, and Dielectric Absorptions of Certain Substances showing Unusual Atomic Polarisations.*

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Measurements are recorded of the above properties for a number of substances which were once thought to display anomalous dipole moments. The new results indicate that the solutes are in fact non-polar, consistently with their structures, each having a centre of symmetry, and with the differences between total polarisations and molecular refractions due to atomic polarisations, as explained earlier by Coop and Sutton.

THIS paper mainly concerns examples of that group of substances which *as solutes* display apparent permanent polarity, by an excess of total polarisation over molecular refraction, but which *as gases* show non-polarity, through a temperature invariance of the total polarisation. Outstanding instances are afforded by the acetylacetone complexes of beryllium, aluminium, copper, iron, cobalt, chromium, and thorium,[1, 2] the apparent moments of which, measured in solution, lie between 1 and 1·8 D. Compounds such as *p*-benzoquinone,[3, 5, 8] carbon suboxide,[5] tetramethyl*cyclo*butane-1 : 3-dione,[7, 8, 9] *p*-dinitrobenzene,[4, 6] etc., similarly exhibit apparent polarity but of a lower order (0·6—0·8 D; cf. also ref. 10). These anomalies have been satisfactorily explained by Coop and Sutton [9] on the basis that the $(P - R)$ values observed by experiment are unexpectedly large atom polarisations; nevertheless the data now to be reported, which have been accumulated over the last ten years, have some interest in certain cases, and in general support the theory just mentioned.

EXPERIMENTAL

Solutes.—The metallic acetylacetone complexes were prepared by methods cited by Finn, Hampson, and Sutton.[2] Nickel–benzoylacetone was a gift from Dr. D. P. Mellor. The m. p.s were in accord with those in the literature. Finn *et al.*[2] do not give a m. p. for copper bisacetylacetone complex, which after crystallisation from dioxan formed blue needles, subliming at 230°; in view of suspicions that in the process combination with the solvent may have occurred, the product was analysed (Found : Cu, 24·0; C, 45·6; H, 5·2. Calc. for $C_{10}H_{14}O_4Cu$: Cu, 24·3; C, 45·8; H, 5·4%). Nitroso-β-naphthol was obtained as described by Vogel,[11] and its iron and cobalt derivatives by the directions of Nicolardot and Valli-Douau [12] and Paulais and Marhuenda [13] respectively; alternatively to the latter the addition of aqueous tetramminocarbonatocobalt to an acetone solution of 1-nitroso-2-naphthol gave a dark red precipitate which analysis showed to be the desired complex. Diphenylmercury was a commercial specimen; after crystallisation from carbon tetrachloride it had m. p. 124·5°.

Solvents.—Carbon tetrachloride and benzene were as specified by Le Fèvre and Le Fèvre.[14] Dioxan was refluxed over sodium for 3 days, and then fractionally distilled through a Widmer column, the fraction of b. p. 100—101°/760 mm. being collected and stored over sodium; immediately before use a portion was redistilled over fresh sodium.

Apparatus, Methods, etc.—Dielectric constants have been determined on the circuit described recently,[15] which now replaces that formerly utilised here; techniques have otherwise conformed

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[1] Angus and Smith, *Proc. Roy. Soc.*, 1932, *A*, **137**, 372.
[2] Finn, Hampson, and Sutton, *J.*, 1938, 1254.
[3] Hassel and Naeshagen, *Z. physikal. Chem.*, 1930, **6**, *B*, 441.
[4] Le Fèvre and Le Fèvre, *J.*, 1935, 957.
[5] *Idem, ibid.*, p. 1696.
[6] Jenkins, *J.*, 1936, 862.
[7] Angus, Leckie, Le Fèvre, Le Fèvre, and Wassermann, *J.*, 1935, 1751.
[8] Hammick, Hampson, and Jenkins, *J.*, 1938, 1263.
[9] Coop and Sutton, *J.*, 1938, 1269.
[10] Le Fèvre, " Dipole Moments," 3rd Edn., Methuen, London, 1953, pp. 21—25.
[11] Vogel, " Practical Organic Chemistry," Longmans, London, 1948, p. 833.
[12] Nicolardot and Valli-Douau, *Bull. Soc. chim. France*, 1918, **23**, 455.
[13] Paulais and Marhuenda, *ibid.*, 1951, **18**, 206.
[14] Le Fèvre and Le Fèvre, *J.*, 1954, 1577.
[15] Buckingham, Chau, Freeman, Le Fèvre, Rao, and Tardif, *J.*, 1956, 1405.

TABLE 1. *Physical properties of solvents employed and derived constants required for calculations.*

Solvents	ε^{25}	d_4^{25}	n_D^{25}	$10^7B_D^{25}$	p	C	H	J	$10^{14}\,{}_sK_1$
CCl_4	2·2270	1·58454	1·4575	0·070	0·18319	0·10596	2·060	0·4731	0·749
Dioxan...	2·2090	1·0280	1·4202	0·068	0·27942	0·16473	2·008	0·4752	1·162
Benzene	2·2725	0·87378	1·4973	0·410	0·34086	0·18809	2·114	0·4681	7·56

TABLE 2. *Observed Kerr constants, refractive indexes dielectric constants and densities of solutions at 25°.*

Diphenylmercury in carbon tetrachloride.

10^5w_2	154	166	180	494	512	614	624
$10^7\Delta B$	0·004	0·004	0·004	—	0·011	0·012	—
n_D^{25}	1·4576	1·4577	1·4578	—	1·4584	—	—
ε^{25}	—	—	—	2·2297	—	—	—
d_4^{25}	—	—	—	1·5866	—	—	1·5872

10^5w_2	728	984	1056	1140	1153	1332	1453
ε^{25}	2·2316	2·2331	2·2335	—	—	2·2338	2·2348
d_4^{25}	1·5877	1·5887	1·5892	1·5895	1·5894	1·5897	1·5909

Whence $\Sigma\Delta B/\Sigma w_2 = 2{\cdot}15$; $\Sigma\Delta n/\Sigma w_2 = 0{\cdot}148$; $\Sigma\Delta\varepsilon/\Sigma w_2 = 0{\cdot}600$; $\Sigma\Delta d/\Sigma w_2 = 0{\cdot}423_3$.

Beryllium bisacetylacetone complex in carbon tetrachloride.

10^5w_2	663	985	1135	1598
$10^6\Delta B$	. . . all *ca.* 0 . . .			
n_D^{25}	1·4584	1·4588	1·4590	1·4597
ε^{25}	2·2367	2·2414	2·2436	2·2505
d_4^{25}	1·57980	1·57749	1·57642	1·57311

Whence $\Sigma\Delta n/\Sigma w_2 = 0{\cdot}1347$; $\Sigma\Delta d/\Sigma w_2 =$ $= 0{\cdot}7154$; $\Sigma\Delta\varepsilon/\Sigma w_2 = 1{\cdot}465$.

Aluminium trisacetylacetone complex in benzene.

10^5w_2	738	1369	2·58	3236
$10^7\Delta B$	*ca.* 0	*ca.* 0	0·001	−0·001
n_D^{25}	—	—	1·4981	1·4986
ε^{25}	2·2791	2·2840	2·2915	2·2999
d_4^{25}	0·87558	0·87704	0·87898	0·88155

Whence $\Sigma\Delta B/\Sigma w_2 =$ *ca.* 0; $\Sigma\Delta n/\Sigma w_2 = 0{\cdot}039$; $\Sigma\Delta\varepsilon/\Sigma w_2 = 0{\cdot}860$; $\Sigma\Delta d/\Sigma w_2 = 0{\cdot}240$.

Aluminium trisacetylacetone complex in dioxan.

10^5w_2	673	895	896	930	1632	2108	2666
$10^7\Delta B$	*ca.* 0	0·0005	0·0005	0·0005	0·001	0·002	0·003
n_D^{25}	1·4212	1·4217	—	—	1·4222	—	1·4231
ε^{25}	—	—	2·2167	2·2172	—	—	—
d_4^{25}	1·0288	1·0290	—	—	1·0300	—	1·0313

Whence $\Sigma\Delta B/\Sigma w_2 = 0{\cdot}077$; $\Sigma\Delta\varepsilon/\Sigma w_2 = 0{\cdot}871$; $\Sigma\Delta d/\Sigma w_2 = 0{\cdot}1210$; $\Sigma\Delta n/\Sigma w_2 = 0{\cdot}126$.

Copper bisacetylacetone complex in dioxan.

10^5w_2	380·5	396·0	405·6	436·2	484·4	531·9	569·1
$10^7\Delta B$	—	—	*ca.* 0	*ca.* 0	*ca.* 0	*ca.* 0	—
n_D^{25}	—	—	—	1·4208	—	1·4210	—
ε^{25}	2·2122	2·2131	2·2131	2·2133	2·2136	—	2·2140
d_4^{25}	$1{\cdot}0290_5$	1·0291	1·0292	1·0292	1·0294	1·0295	1·0295

Whence $\Sigma\Delta n/\Sigma w_2 = 0{\cdot}145$; $\Sigma\Delta d/\Sigma w_2 = 0{\cdot}2793$; $\Sigma\Delta\varepsilon/\Sigma w_2 = 0{\cdot}947$.

Nickel bisbenzoylacetone complex in dioxan.

10^5w_2 ...	541·1	897·3	905·5	944·3	1058·0	1094·7	1149·0	1156·0	1509·9
n_D^{25}	—	—	1·4212	1·4218	—	1·4220	—	—	—
ε^{25}	2·2155	2·2205	2·2206	2·2209	2·2213	2·2215	2·2211	2·2209	2·2234
d_4^{25}	1·02943	1·0304	1·0303	1·03045	1·0305	1·0307	1·0308	1·0308	1·0320

Whence $\Sigma\Delta\varepsilon/\Sigma w_2 = 1{\cdot}11_3$; $\Sigma\Delta d/\Sigma w_2 = 0{\cdot}253$; $\Sigma\Delta n/\Sigma w_2 = 0{\cdot}149$.

1-*Nitroso-2-naphthol in benzene.*

10^5w_2	962	1115	1404	1485	1615	1823
ε^{25}	2·3878	2·4099	2·4385	2·4496	2·4704	2·4962
d_4^{25}	0·87649	0·87694	0·87776	0·87815	0·87844	0·87904

Whence $\Sigma\Delta\varepsilon/\Sigma w_2 = 12{\cdot}0$; $\Sigma\Delta d/\Sigma w_2 = 0{\cdot}2873$.

Ferric 1-*nitroso-2-naphthoxide in benzene.*

10^6w_2	860	876	960	962
ε^{25}	2·2744	2·2745	2·2743	2·2743
d_4^{25}	0·87417	0·87414	0·87416	0·87421

Whence $\Delta\Sigma\varepsilon/\Sigma w_2 = 2{\cdot}0_5$; $\Sigma\Delta d/w_2 = 0{\cdot}426_5$.

Cobalt 1-*nitroso-2-naphthoxide in benzene.*

10^6w_2	662	735	780	985
ε^{25}	2·2740	2·2743	2·2751	2·2749
d_4^{25}	0·87404	0·87402	0·87412	—

Whence $\Sigma\Delta\varepsilon/\Sigma w_2 = 2{\cdot}6_3$; $\Sigma\Delta d/\Sigma w_2 = 0{\cdot}386$.

TABLE 3. *Calculation of molar Kerr constants, polarisations, refractions, and apparent moments.*

Solute *	Solvent	$\alpha\varepsilon$	β	γ	δ	$_\infty(_mK_2)$	$_\infty P_2$ (c.c.)	R_D (c.c.)	μ (D)
$HgPh_2$ ...	CCl_4	0·600	0·267	0·102	30·7	82·5	70·2	64·7	(0·52)
BeA_2	CCl_4	1·465	$-0{\cdot}451_5$	0·092	*ca.* 0	1·0	87·3	60	$(1{\cdot}1_5)$
AlA_3	C_6H_6	0·86	$0{\cdot}27_5$	0·026	*ca.* 0	7·2	132·6	91	$(1{\cdot}4_3)$
AlA_3	Dioxan	0·871	0·118	0·089	1·2	6·0	126·5	91	$(1{\cdot}3_2)$
CuA_2	Dioxan	0·947	0·272	0·102	*ca.* 0	0·53	94·1	66	$(1{\cdot}1_7)$
$Ni(BA)_2$...	Dioxan	1·113	0·246	0·105	—	—	151·3	100	(1·6)
H(NN) ...	C_6H_6	12·0	0·329	—	—	—	430·5	46·4 †	4·33
$Fe(NN)_3$...	C_6H_6	$2{\cdot}0_5$	0·488	—	—	—	321	171 ‡	2·7
$Co(NN)_3$...	C_6H_6	2·63	0·442	—	—	—	394	170 ‡	3·3

* A, BA, and NN respectively stand for the residues of acetylacetone, benzoylacetone, and 1-nitroso-2-naphthol.

† Calc. from $_\infty P_2(C_{10}H_8) = 44{\cdot}0$ (Le Fèvre and Le Fèvre[19]) together with $R_{CH} = 1{\cdot}68$, $R_{OH} = 1{\cdot}80$, $R_{NO} = 4{\cdot}0$ from Vogel *et al.*[20] ‡ From Higasi.[21]

TABLE 4. *Frequency differences in Mc./sec. at half-height of resonance curve.**

Diphenylmercury in CCl_4 *at* 12°.

10^5w_2	0	785	830	1260
Δf	0·80	0·79	0·80	0·79

Beryllium acetylacetone complex † *in* CCl_4 *at* 20°.

10^5w_2	0	985	1135	1598
Δf	0·82	0·81	0·82	0·81

Aluminium acetylacetone complex † *in* C_6H_6 *at* 19°.

10^5w_2	0	1369	2158
Δf	1·07	1·08	1·07

Cobalt acetylacetone complex † *in* C_6H_6 *at* 13°.

10^5w_2	0	756	817
Δf	1·05	1·05	1·04

Copper acetylacetone complex in dioxan at 20°.

10^5w_2	0	406	484	569
Δf	3·79	3·80	3·81	3·80

Nickel benzoylacetone complex in dioxan at 20°.

10^5w_2	0	905·5	1118	1466
Δf	3·87	4·00	4·05	4·08

p-*Benzoquinone* † *in benzene at* 20°.

10^5w_2	0	430	527
Δf	1·07	1·08	1·07

* See ref. 18 for details, and also for examples of Δf values produced by polar solutes.

† Observations recorded during 1952–53 by Dr. E. P. A. Sullivan.

to those described in ref. 10. Electric double-refraction measurements were made with the equipment cited in ref. 16, and those of Δ tan δ with that cited in ref. 18. The symbols used below, and methods of computation employed, have been defined in refs. 10 and 15—18.

Observations.—Certain necessary properties of the three solvents involved are given as Table 1; observations concerned with Kerr effects and polarisations of solutions follow as Table 2; calculations of molar Kerr constants and total polarisations at infinite dilution, $_\infty(_mK_2)$ and $_\infty(P_2)$ respectively, together with molecular refractions R_D and moments μ (" apparent " moments being indicated by parentheses), are in Table 3. Table 4 records the details of the dielectric-loss (" *Q* factor ") determinations.

DISCUSSION

Diphenylmercury.—The present appear to be the first measurements of the polarisation of this solute in carbon tetrachloride. The figures obtained (70·2 c.c.) compare satisfactorily with those recorded in other media :

68·8 c.c. in benzene at 25° (Hampson[22])
69·3 c.c. in decalin at 25° (Hampson[22])
69·02 c.c. in dioxan at 25° (Curran and Wenzke[23])
72·12 c.c. in dioxan at 20° (Sipos, Sawatzky, and Wright[24])

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[16] Le Fèvre and Le Fèvre, *J.*, 1953, 4041.

[17] Le Fèvre and Le Fèvre, *Rev. Pure Appl. Chem.*, 1955, **5**, 261.

[18] Le Fèvre and Sullivan, *J.*, 1954, 2873.

[19] Le Fèvre and Le Fèvre, *J.*, 1955, 1641.

[20] Vogel, Cresswell, Jeffery, and Leicester, *J.*, 1952, 514.

[21] Higasi, *Bull. Inst. Phys. Chem. Res. Tokyo*, 1932, **11**, 729.

[22] Hampson, *Trans. Faraday Soc.*, 1934, **30**, 877.

[23] W. J. Curran and Wenzke, *J. Amer. Chem. Soc.*, 1935, **57**, 2162.

[24] Sipos, Sawatzky, and Wright, *ibid.*, 1955, **77**, 2759.

An earlier determination in benzene, by Bergmann and Schutz,[25] has been criticised by Hampson.[22] The apparent moments calculable from these data depend upon the assumptions made concerning the distortion polarisation. Hampson, and Curran and Wenzke, took the R_D observed in benzene (65·3 c.c.) as ${}_{D}P$, whence μ = *ca.* 0·4 D. Sipos *et al.*[24] used the total polarisation found for the *solid* (compressed in pellet form), *viz.*, 59·2 c.c., whence μ = 0·79 D. We consider 59·2 c.c., however, to be too low—it is *below* the R_D's reported by Hampson for benzene, by us for carbon tetrachloride, and by Wilde[26] for pyridine and " Westron " (tetrachloroethane) solution. In this connection it is interesting that Wüsthoff[27] has given 12·7—13·0 c.c. as the total polarisation of mercury vapour; from this value in conjunction with 25·36 c.c. listed by Vogel[28] for the phenyl group we might expect the molecular refraction of diphenylmercury to be 63·4—63·7 c.c. A similar conclusion is reached by using R_D (Hg) = 12·84 c.c. noted by Jones, Evans, Gulwell, and Griffiths[29] for combined mercury. If we adopt $R_D(\mathrm{HgPh_2})$ = 64·7 c.c., the polarisation given by Sipos, Sawatzky, and Wright corresponds to μ = 0·60 D.

Our present results have a bearing on the configuration of diphenylmercury. By theory,[30] since the mercury valency electrons occupy $6s^2$ orbitals, all substances of the type X–Hg–X should be rectilinear, and for the vapourised and the solid state the greater part of the available experimental evidence indicates that this is so.[31] In particular, *X*-ray examination of crystalline diphenylmercury indicated a Ph–Hg–Ph angle of 180° with the molecule planar and centrosymmetrical.[32]

Unfortunately, observations made on *solutions* of mercury compounds have not been so easily interpretable, and why the dissolved mercuric dihalides show considerable dipole moments is not yet entirely clear.[23, 33-35] Smyth,[36] and Oesper and Smyth,[37] took the C–Hg–Cl angle as 180° in benzylmercuric chloride although Curran[34] considered certain arylmercuric bromides to be non-linear. Hampson[22] raised the possibility that the apparent polarity of diphenylmercury is due to the thermal agitation of a flexible structure, while more recently Sipos, Sawatzky, and Wright[24] suggested that Ph–Hg–Ph is permanently bent, with C–Hg–C angles between 130° and 150°.

In view of the last suggestion the fact that diphenylmercury causes no detectable dielectric loss when dissolved in carbon tetrachloride is significant. There is no case on record in which a polar and anisotropic solute has failed to exhibit a measurable relaxation time.[38] We conclude therefore that this molecule has in fact no permanent dipole moment.

The anisotropic polarisability of diphenylmercury is revealed by the magnitude of the molar Kerr constant now recorded. *A priori* estimates of the ${}_{m}K$'s to be expected for different configurations may be made as follow : let $R_\infty(\mathrm{HgPh_2})$ be taken as *ca.* 63·0 c.c., and *R* for phenyl[20] as 24·3 c.c. The refraction of the C–Hg link is accordingly 6·7 c.c., and b_L(C–Hg) + $2b_T$(C–Hg) = 0·795 × 10^{-23}. For the phenyl group, $b_1 = b_2 =$ (1·114—0·0635) × 10^{-23} and $b_3 = (0·733 - 0·0635) \times 10^{-23}$ (see ref. 17). In the absence of precise information, it is a reasonable assumption that for the bond joining phenyl with

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[25] Bergmann and Schutz, *Z. physikal. Chem.*, 1932, **19**, *B*, 401.

[26] Wilde, *J.*, 1949, 72.

[27] Wüsthoff, *Ann. Physik*, 1936, **27**, 312.

[28] Vogel, *J.*, 1948, 1842.

[29] Jones, Evans, Gulwell, and Griffiths, *J.*, 1935, 39.

[30] Pauling, " The Nature of the Chemical Bond," Cornell Univ. Press, New York, 1945, Chap. 3.

[31] See refs. in *Ann. Reports*, 1952, **49**, 367; Braune and Linke, *Z. physikal. Chem.*, 1935, **31**, *B*, 12; Braekken and Scholten, *Z. Krist.*, 1934, **89**, 448; Kohlrausch, " Der Smekal-Raman Effekt," Springer, Berlin, 1931, pp. 182—4; Krishnamurti, *Indian J. Phys.*, 1903, **5**, 113; Braune and Engelbrecht, *Z. physikal. Chem.*, 1930, **10**, *B*, 1; 1931, **11**, *B*, 409; Braune and Knoke, *ibid.*, 1933, **23**, *B*, 163; Allen and Sutton, *Acta Cryst.*, 1950, **3**, 46; Gregg, Hampson, Jenkins, Jones, and Sutton, *Trans. Faraday Soc.*, 1937, **33**, 852.

[32] Kitaigorodski and Grdenic, *Izvest. Akad. Nauk S.S.S.R.*, 1948, **2**, 262.

[33] Bell, *J.*, 1931, 1371.

[34] B. C. Curran, *J. Amer. Chem. Soc.*, 1941, **63**, 1470; 1942, **64**, 830.

[35] Crenshaw, Cape, Finkelstein, and Roger, *ibid.*, 1938, **60**, 2308.

[36] Smyth, *J. Org. Chem.*, 1941, **6**, 421.

[37] Oesper and Smyth, *J. Amer. Chem. Soc.*, 1942, **64**, 173.

[38] Davies, *Quart. Rev.*, 1954, **8**, 250.

mercury the $b_L : b_T$ ratio lies between 2 and 3·5. The polarisability semiaxes and therefore the molar Kerr constants for diphenylmercury in its rectilinear form with the phenyl groups respectively coplanar or orthogonal then emerge ($\times 10^{12}$) as :

$b_L : b_T$ ratio	${}_mK$ (coplanar)	${}_mK$ (orthogonal)	${}_mK$ (expt.)
2	53·4	31·1	82·5
3	75·4	53·1	
3·5	84·9	57·4	

In these computations a zero $\mu_{\text{resultant}}$ has, of course, been used, so that $\theta_2 = 0$ (see ref. 17, p. 270). Indications are therefore that the correct $b_L : b_T$ ratio is around 3·5, whence for the C_{Ar}–Hg link $b_L = 0{\cdot}506$ and $b_T = 0{\cdot}144_5 \times 10^{-23}$ c.c.

The Metallic Acetylacetone Complexes.—In the two cases where dielectric polarisations have been measured in the solvents used by Finn, Hampson, and Sutton,[2] confirmatory figures have been obtained :

Beryllium acetylacetone complex : 87·3 c.c. in CCl_4 at 25° ; Finn *et al.* give 87·7 c.c.

Aluminium acetylacetone complex : 132·6 c.c. in C_6H_6 at 25° ; Finn *et al.* give 134·0 c.c.

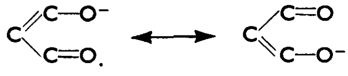
Finn *et al.* include no data for solutes in dioxan. The aluminium derivative in this medium yields a value (126·5 c.c.) which approaches that (122·3 c.c.) found by Finn *et al.* in chloroform. By contrast, the compound of copper shows a definitely larger polarisation in dioxan (94·1 c.c.) than in chloroform [2] (67·7 c.c.) ; similarly the ${}_\infty P_2$ of beryllium acetylacetone complex is reduced from 87—88 c.c. in carbon tetrachloride to 64·8 c.c. in chloroform.[2]

None of the above substances causes dielectric loss (see Table 4) in the solvent named against it in Table 3, in accord with the intrinsic non-polarity demonstrated by Coop and Sutton.[9] The small positive molar Kerr constants of the beryllium and aluminium compounds can also be viewed as being in harmony with the ideas of Coop and Sutton,[9] since with tetrahedral or octahedral arrangements of the two or three bidentate ligands respectively near-isotropy is to be expected.

Copper acetylacetone complex presents a problem. If—as is commonly believed—it has the planar " square " configuration, considered from Cox and Webster's report [39] to exist in the crystal, it should show a larger positive ${}_mK$ than its beryllium or aluminium relative; actually its ${}_mK$ in dioxan is smaller than either. Such a contrast between the complex as a solid and as a solute might arise from one or two, or perhaps a combination of two, effects. The act of dissolution might change (*a*) the *configuration,* or (*b*) the *constitution* of the individual molecules.

Regarding possibility (*a*), it is obvious that were the valency configuration of copper modified from square coplanar in the crystal to tetrahedral in solution, the observed phenomenon would be explicable. However the greater strength (2·694 compared with 2) of dsp^2 than of sp^3 bonds is here involved and it seems doubtful whether energy changes associated with the process of dissolution could adequately facilitate the rearrangement.

Alternatively, even with a planar bond distribution around the copper, a high degree of isotropy for the complex as a whole could be achieved by " buckling " each of the acetylacetone residues, one above and the other below the " copper plane." Yet, were this to occur, it would have some effect on the bonding of the chelate to the metal, for the three carbon atoms of the C=C–C unit would be out of the plane of the two carbon–oxygen links, and the effective enolate resonance :



would be reduced. Such resonance is not confined to the ligand alone but includes the lower-orbital electrons of the copper atom. Now, Calvin and Wilson [40] have pointed out that enolate resonance plays a far greater part in the bonding of copper than it does in that of hydrogen, and that this extra bonding is closely affected by any changes of resonance in

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[39] Cox and Webster, *J.*, 1935, 731.

[40] Calvin and Wilson, *J. Amer. Chem. Soc.*, 1945, **67**, 2003.

the ligand. In the particular instance under discussion, non-planarity of the ligand should reduce the resonance with the copper and cause the bonding to resemble that between the ligand and hydrogen. That the last is not the case is clear from stability-constant measurements[40] of copper bisacetylacetone complex and acetylacetone in water–dioxan solutions of equal acidity: the constant of the copper complex is far greater than that of the corresponding hydrogen " complex." For these reasons therefore it seems unlikely that the low birefringence of the copper derivative is due to distorted ligands.

Possibility (*b*) is, on known facts, more plausible. The co-ordination of two dioxan molecules above and below the copper would form a solvation complex for which a low anisotropy is conceivable. There is some evidence for the existence of sexacovalent Cu^{II} complexes in solution,[41] and copper bisacetylacetone complex forms a bright green compound with ammonia,[42] the composition of which is stated to be $Cu(C_5H_7O_2)_2,2NH_3$. The actual isolation[43] of dioxan complexes of the mercuric halides, and the *X*-ray crystallographic examination[44] of one of them, show that dioxan can behave as a donor. If the present suggestion is correct, the dioxan must be weakly attached, since all attempts to secure a solid dioxan complex of $Cu(C_5H_7O_2)_2$ have been unsuccessful.

Finally, it is relevant to mention that the magnetic moment (1·95 B.M.) listed by Sugden[45] for copper acetylacetone complex may—if sufficiently reliable—be interpreted by the argument of Ray and Sen[46] to indicate a tetrahedral disposition of the valency bonds of copper in the complex; such, of course, is contrary to Cox and Webster's conclusions (which require a moment of *ca.* 1·8 B.M.).

Nickel Bisbenzoylacetone Complex.—Since the assignment of bivalent nickel complexes to the tetrahedral or square-coplanar classes can be determined magnetically, the susceptibility of this complex was examined by the Gouy method as a preliminary. It proved to be paramagnetic with a moment of 3·1 B.M., corresponding to two unpaired electrons. Configurationally therefore it is tetrahedral (cf. Pauling[30] and Mellor *et al.*[47]).

Owing to the fact that it contains two methyl and two phenyl groups it should exhibit a small resultant electric moment, and the whole of the $P - R$ difference, given in Table **3**, may not therefore be recognised as atomic polarisation. Consistently with this, dielectric-loss measurements (in dioxan) indicated a non-zero relaxation time, which could not however be computed owing to ignorance of the true dipole moment.

Unfortunately the solutions were too intensely coloured to allow electric double-refraction observations; the same objection prevented work on the acetylacetone complexes of chromium and cobalt.

*The Tris-*1-*nitroso-*2-*naphthoxides of Cobalt and Iron.*—These require little comment. They were prepared in the hope that their $_mK$'s could be studied, but again their strong colours prevented this. Higasi[21] in 1932 had reported electric moments of 3·1 and 3·8 D for the iron and the cobalt complex respectively, but owing to sparing solubility the concentrations examined were extremely low, and changes in ε and d correspondingly small. During the present redeterminations therefore, the weight fractions of solute in the solutions have been ascertained both by weighing during making up, and by weighing of the residue after evaporation of a weighed quantity of solution. The polarities now obtained are lower than those given by Higasi.

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