179. *Molecular Polarisability: the Apparent Polarities and Molar Kerr Constants of Seven Quinones.*

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The molar Kerr constants observed for *p*-benzoquinone, chloranil, and anthraquinone can be explained consistently with the Sutton–Coop treatment of anomalous apparent polarity, if in each of these centrosymmetric molecules the ratios of the principal electrostatic and electro-optical polarisabilities are not uniform. Satisfactory predictions of molar Kerr constants for phenanthraquinone, acenaphthaquinone, and camphorquinone can be based on previously determined bond anisotropies and conventional intervalency angles. A permanent moment acting across the 2,3-link is indicated in 1,4-naphthaquinone, analogous to that supposed by Hampson and Weissberger in 1,4-dichloronaphthalene.

THE problem of explaining the " anomalous " apparent polarities of benzoquinone [1-3] and other [4] centrosymmetric molecules has lately been revived by Paoloni [5] who, after reviewing relevant publications before 1958 (including papers by Kofod,[6] Meredith *et al.*,[7]

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[1] Hassell and Naeshagen, *Z. phys. Chem.*, 1929, *B*, **6**, 445.
[2] Le Fèvre and Le Fèvre, *J.*, 1935, 1696.
[3] Hammick, Hampson, and Jenkins, *Nature*, 1935, **136**, 990; *J.*, 1938, 1263.
[4] Le Fèvre, " Dipole Moments," Methuen, London, 3rd edn., 1953, pp. 21—25.
[5] Paoloni, *J. Amer. Chem. Soc.*, 1958, **80**, 3879.
[6] Kofod, *Acta Chem. Scand.*, 1953, **7**, 928.
[7] Meredith, Westland, and Wright, *J. Amer. Chem. Soc.*, 1957, **79**, 2835.

Jenkins,[8] Frank and Sutton,[9] and Coop and Sutton,[10] *X*-ray studies by Robertson,[11] and electron diffraction measurements by Swingle [12] and by Kimura and Shibata [13]) comments that, although the experimental evidence at present available favours a planar structure of benzoquinone, the possibility of small deviations from planarity cannot be ruled out. Le Fèvre and associates [14,15] have accepted the concept of vibration polarisation ever since it was first suggested by Coop and Sutton,[10] and therefore have not especially sought for signs of slow or permanent distortions among this " anomalous " group of compounds. Accordingly, the observation that solutions of benzoquinone in benzene showed dielectric losses not detectably greater than those of benzene alone was recorded without remark,[15] and preliminary findings (by Mrs. C. G. Le Fèvre) that the same solute very slightly raised the Kerr effect of benzene were left undeveloped.

Charney [16] recently reported experiments to test Paoloni's proposal [5] that, under the external electric field used in dielectric-constant determination, the electron clouds around the oxygen atoms in benzoquinone can be deformed to create a charge dissymmetry much larger than that associated with normal electronic polarisation, so that a planar arrangement of the nuclei may possess a dipole moment responsible for " substantial molecular orientation in an electric field." *Inter alia*, Charney, therefore compared the Kerr constants of benzene and benzoquinone solutions. He states that " within the limits of precision of the measurements " the birefringences are the same. In view of the slightly different exploratory indications mentioned above, further work seemed justified; the enquiry has also been extended to include three other quinones which, like benzoquinone, might on elementary principles be expected to have zero polarity.

EXPERIMENTAL

Materials, Apparatus, Methods, etc., and Results.—Benzo- and naphtha-quinones were purified by steam-distillation and recrystallisation twice from benzene, and had m. p. 116° and 125°, respectively. Chloranil, after recrystallisation from toluene, had m. p. 289—290°. Anthraquinone and acenaphthaquinone were first extracted and then recrystallised twice from benzene, and had m. p. 280—283° and 260—261°, respectively. Starting materials were commercial specimens in each case.

Descriptions of apparatus, details of calculations, and definitions of symbols used here, are set out in refs. 4, 17, and 18, and relisted in ref. 19. Observations and results are given under usual headings in Tables 1—3.

DISCUSSION

Apparent Polarisations and Moments.—Table 1 contains new total polarisation measurements for chloranil, 1,4-naphthaquinone, anthraquinone, and acenaphthaquinone. Chloranil exhibits about the same difference between $_{\infty}P_2$ and R_D as does benzoquinone; with anthraquinone the excess is less. In Table 2, apparent moments are evaluated by assuming that the distortion polarisations are $1{\cdot}05R_D$. Since Meredith *et al.*[7] claim that the total polarisation of benzoquinone pelletted to maximum density is only 30·1 c.c., perhaps $_DP$ is approximately equal to R_D, in which case the three moments less than unity will be raised somewhat. Putting $_DP = R_D$ does not significantly affect the μ's estimated for

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[8] Jenkins, *J.*, 1936, 864, 910.

[9] Frank and Sutton, *Trans. Faraday Soc.*, 1937, **33**, 1307.

[10] Coop and Sutton, *J.*, 1938, 1269.

[11] Robertson, *Proc. Roy. Soc.*, 1935, *A*, **150**, 106.

[12] Swingle, *J. Amer. Chem. Soc.*, 1954, **76**, 1409.

[13] Kimura and Shibata, *Bull. Chem. Soc. Japan*, 1954, **27**, 163.

[14] Le Fèvre and Narayana Rao, *Austral. J. Chem.*, 1954, **7**, 135; 1955, **8**, 39.

[15] Armstrong, Le Fèvre, and Le Fèvre, *J.*, 1957, 371.

[16] Charney, *J. Amer. Chem. Soc.*, 1961, **83**, 578.

[17] Le Fèvre and Le Fèvre, (*a*) *Rev. Pure Appl. Chem.*, 1955, **5**, 261; (*b*) " Physical Methods of Organic Chemistry," Part 3 of " Technique of Organic Chemistry," ed. A. Weissberger, Interscience Publ., Inc., New York, 3rd edn., 1960.

[18] Buckingham, Chau, Freeman, Le Fèvre, Rao, and Tardif, *J.*, 1956, 1405.

[19] Le Fèvre and Sundaram, *J.*, 1962, 1494.

TABLE 1.

Dielectric constants, densities, refractive indexes, and Kerr effects of some quinones in benzene * at 25°.

Solute: *p*-Benzoquinone.

$10^5 w_2$...	593	699	938	1142
$10^{10}\Delta B$	11	13	15	19

whence $\Sigma\Delta B/\Sigma w_2 = 1{\cdot}720 \times 10^{-7}$

Solute: Chloranil.

$10^5 w_2$...	412	720	986	1254	1702	1779
$10^4\Delta n$...	3	5	7	9	12	13
$10^4\Delta n^2$	9	15	21	27	36	39
$10^5\Delta d$...	192	333	455	583	793	826
$10^4\Delta\varepsilon$...	17	30	42	53	71	75
$10^{10}\Delta B$...	4	8	11	14	18	20

whence $\Sigma\Delta n/\Sigma w_2 = 0{\cdot}071_5$; $\Sigma\Delta n^2/\Sigma w_2 = 0{\cdot}214_5$; $\Sigma\Delta d/\Sigma w_2 = 0{\cdot}4643$; $\Sigma\Delta\varepsilon/\Sigma w_2 = 0{\cdot}420_3$; $\Sigma\Delta B/\Sigma w_2 = 1{\cdot}09_4 \times 10^{-7}$.

Solute: 1,4-Naphthaquinone.

$10^5 w_2$...	348	682	921	1164	1255	1299
$10^1\Delta n$...	3	6	8	10	11	12
$10^4\Delta n^2$	9	18	24	30	33	35
$10^5\Delta d$...	94	183	248	314	339	349
$10^4\Delta\varepsilon$...	53	104	141	179	195	198
$10^{10}\Delta B$	12	23	30	39	43	44

whence $\Sigma\Delta n/\Sigma w_2 = 0{\cdot}088$; $\Sigma\Delta n^2/\Sigma w_2 = 0{\cdot}263$; $\Sigma\Delta d/\Sigma w_2 = 0{\cdot}2694$; $\Sigma\Delta\varepsilon/\Sigma w_2 = 1{\cdot}535$; $\Sigma\Delta B/\Sigma w_2 = 3{\cdot}37 \times 10^{-7}$.

Solute: Anthraquinone.

$10^5 w_2$...	119	191	245	269
$10^5\Delta n$...	17	26	35	41
$10^5\Delta n^2$	51	78	104	122
$10^5\Delta d$...	36	64	78	82
$10^4\Delta\varepsilon$...	6	11	12	15
$10^{10}\Delta B$	4	6	8	9

whence $\Sigma\Delta n/\Sigma w_2 = 0{\cdot}144$; $\Sigma\Delta n^2/\Sigma w_2 = 0{\cdot}431$; $\Sigma\Delta d/\Sigma w_2 = 0{\cdot}3155$; $\Sigma\Delta\varepsilon/\Sigma w_2 = 0{\cdot}534$; $\Sigma\Delta B/\Sigma w_2 = 3{\cdot}28 \times 10^{-7}$.

Solute: Acenaphthaquinone.

$10^5 w_2$...	97	103	133	142	164	183
$10^5\Delta d$...	27	32	39	45	—	55
$10^4\Delta\varepsilon$...	212	239	275	329	—	405
$10^{10}\Delta B$	94	101	136	138	158	182

whence $\Sigma\Delta d/\Sigma w_2 = 0{\cdot}3005$; $\Sigma\Delta\varepsilon/\Sigma w_2 = 22{\cdot}16$; $\Sigma\Delta B/\Sigma w_2 = 98{\cdot}31 \times 10^{-7}$.

Solute: Acenaphthaquinone. Solvent: Quinoline.†

$10^5 w_2$...	432	597	678
$10^4\Delta n^2$	16	26	29
$10^5\Delta d$...	117	164	180

whence $\Sigma\Delta n^2/\Sigma w_2 = 0{\cdot}416$; $\Sigma\Delta d/\Sigma w_2 = 0{\cdot}2701$.

* When $w_2 = 0$, $\varepsilon = 2{\cdot}2725$, $d = 0{\cdot}87378$, $(n_1)_D = 1{\cdot}4973$, and $B_1 = 0{\cdot}410 \times 10^{-7}$.
† When $w_2 = 0$, $(n_1)_D = 1{\cdot}6247_5$, and $d = 1{\cdot}0900$.

TABLE 2.

Total polarisations at infinite dilution, molar refractions and apparent dipole moments calculated from Table 1.

Solute	M_2	$\alpha\varepsilon_1$	β	$\gamma' n_1^2$	$_\infty P_2$ (c.c.)	R_D (obsd.) (c.c.)	μ (D) *
p-Benzoquinone †	108·1	0·529	0·2160	0·107	39·61	30·6	$0{\cdot}60_5$
Chloranil	245·9	$0{\cdot}420_3$	0·5314	$0{\cdot}214_5$	58·72	48·7	0·61
1,4-Naphthaquinone ...	158·2	$1{\cdot}53_5$	0·3083	0·263	83·0	44·6	1·33
Anthraquinone	208·2	0·534	0·3611	0·431	66·25	61·7	0·27
Phenanthraquinone ‡	208·2	$16{\cdot}81_5$	0·3470	0·419	704·8	62·1	5·59
Acenaphthaquinone ...	182·2	22·16	0·3439	—	800·2	—	$6{\cdot}0_3$
			0·2478 d	0·416 §		54·1 §	
Camphorquinone ¶ ...	166·2	23·67	—0·484	0·231	462·0	46·7	4·49

* Distortion polarisation being taken as $1{\cdot}05R_D$. † Data recalc. from Le Fèvre and Le Fèvre.[2] ‡ Data recalc. from Caldwell and Le Fèvre.[20] § Determined in quinoline. ¶ Measurements in CCl_4 by Mr. J. Eckert.[21]

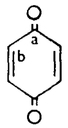
TABLE 3.

Molar Kerr constants at infinite dilution, and exaltations in molar refractions calculated from Tables 1 and 2.

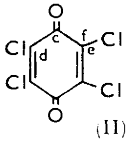
Solute	γ	δ	$_\infty(_mK_2)$	R_D (calc.) (c.c.)	$10^{23}\Delta b$ *
p-Benzoquinone	0·024	4·20	38·5	26·8	0·452
Chloranil	0·048	2·67	53·7	46·1	0·309
1,4-Naphthaquinone	0·059	8·22	97·3	42·1	0·297
Anthraquinone	0·096	8·00	130·4	57·4	0·511
Phenanthraquinone	0·140	170·6	2570	57·4	0·559
Acenaphthaquinone	—	239·8	3169	51·4	0·321
Camphorquinone †	0·053	246	294	44·1	0·309

* Calc. as $10^{23}\Delta b = 0{\cdot}11891$ (R_D obsd. — R_D calc.). † See last footnote of Table 2.

1,4-naphthaquinone or the last three substances in Table 2. The present results for acenaphthaquinone ($_{\infty}P_2$ = 800·2 c.c., μ = 6·03 D) are slightly lower than those recorded [20] in 1939 ($_{\infty}P_2$ = 819·1 c.c., μ = 6·08 D). Regarding 1,4-naphthaquinone, following through the argument used by Hampson and Weissberger [22] on 1,4-dichloronaphthalene with μ(C:O) instead of μ(C–Cl) suggests that part of the 1·33 D is due to permanent polarity directed parallel to the 8,1-line; the $_{\infty}P_2$ of 83·0 c.c. now observed for this quinone compares fairly satisfactorily with 81·0 c.c. found by Soundararajan and Vold [23] at 35°.



(I)



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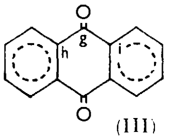

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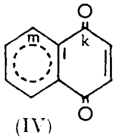

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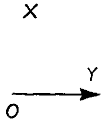

Polarisabilities and Molar Kerr Constants.—By usual procedures,[17,24,25] the principal polarisabilities (b_1, b_2, and b_3) of each of the seven quinones have been calculated from the longitudinal, transverse, and " vertical " polarisabilities (b_L^{AB}, b_T^{AB}, and b_V^{AB}) of the constituent bonds AB (where AB is C–H, C=O, C–C, C=C, or C–Cl) [24] combined with reasonable intervalency angles based upon those available from the *X*-ray analyses [26] of benzoquinone and chloranil. When appropriate, values of b_1, b_2, and b_3 for the C_6H_4 unit, obtained from the corresponding semi-axes for benzene (1·120, 1·120, and 0·736; cf. ref. 27) by subtraction of the isotropic polarisability of two C–H links, have been used with molecules containing fused-rings. Cognisance has been taken of the exaltations of polarisability revealed by comparing refractivities as observed and as computed from the link refractions of Vogel *et al.*[28] (cf. Tables 2 and 3).

We discuss first the four quinones (I—IV) in which the following angles are assumed: a = 116°, b = 122°, c = 110°, d = 125°, e = 123°, f = 112°, g = 117·5°, h = 121·25°, i = 120°, k = 116°, l = 122°, and m = 120°. For reference, let the *X* axis join the carbonyl carbons, and the *Y* axis be at 90° to *X* in the planes corresponding to $C_{(2)}$,$C_{(3)}$,$C_{(5)}$,$C_{(6)}$ in (I); *Z* is perpendicular to *X* and *Y*. For a planar arrangement of *p*-benzoquinone (I) the bond polarisabilities quoted above give: b_1 = 1·465 (along *OX*), b_2 = 0·997 (along *OY*), b_3 = 0·610, and $_{m}K$ calc. = 27·4 × 10^{-12}; with the exaltation divided equally between b_1 and b_2, $_{m}K$ calc. becomes 44·0 × 10^{-12}, while with the exaltation added wholly to b_1, $_{m}K$ cal. is 67·6 × 10^{-12}. Both the last two estimates exceed the observed $_{m}K$. Analogies with other conjugated molecules [24,29] strongly suggest that the exaltation of polarisability is correctly applied in the *OX*-direction; if this is so then the calculated and found $_{m}K$'s can be brought to equality either (*a*) if the electrostatic polarisability along *OZ* is related to b_3 differently from the ways in which the electrostatic polarisabilities along *OX* and *OY* are to b_1 and b_2, or (*b*) if the molecule carries a moment component μ_Z of 0·56 D. Suggestion (*a*) can be reconciled with Paoloni's proposal,[5] with field-induced flexions of the Coop–Sutton [10] type, and with the temperature-invariant θ_3 terms of Le Fèvre and Le Fèvre; [30] for example (writing a_1, a_2, and a_3 for the electrostatic polarisabilities corresponding to b_1, b_2, and b_3; cf. p. 270 of ref. 17*a*), supposing that a_1/b_1 = a_2/b_2 = 1, but that a_3/b_3 = 2, gives a_3 = 1·22 and $_{m}K$ calc. = 38·0 × 10^{-12} (observed,

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[20] Caldwell and Le Fèvre, *J.*, 1939, 1614.
[21] Eckert, M.Sc. Thesis, Sydney, 1961.
[22] Hampson and Weissberger, *J.*, 1936, 393.
[23] Soundararajan and Vold, *Trans. Faraday Soc.*, 1958, **54**, 1155.
[24] Le Fèvre, *J. Proc. Roy. Soc. New South Wales*, 1961, **95**, 1.
[25] Eckert and Le Fèvre, *J.*, 1962, 1081.
[26] Sutton, " Tables of Interatomic Distances and Configuration in Molecules and Ions," *Chem. Soc. Spec. Publ.*, No. 11, 1958.
[27] Aroney and Le Fèvre, *J.*, 1960, 3600.
[28] Vogel, Cresswell, Jeffrey, and Leicester, *J.*, 1952, 514.
[29] Bramley and Le Fèvre, *J.*, 1960, 1820.
[30] Le Fèvre and Le Fèvre, *J.*, 1959, 2670.

$38{\cdot}5 \times 10^{-12}$; of course, many ratios other than 1, 1, and 2 would also illustrate the point). Suggestion (*b*) could have substance if the molecule became *cis*-non-planar long enough for true orientation polarisation to manifest itself; if, as seems likely from the polarities of other conjugated ketones (*e.g.*, piperitone[31] for which $\mu = 3{\cdot}7$—$3{\cdot}8$ D), μ(C:O) in quinones is between 3 and 4 D then the C=O groups of benzoquinone need to be inclined to the *XOY*-plane by only 4—5° to make $_{\mathrm{m}}K$ calc. = $_{\mathrm{m}}K$ found (with a non-planarity of 4·5°, we have $b_1 = 1{\cdot}917$, $b_2 = 0{\cdot}996$, $b_3 = 0{\cdot}615$, μ resultant = 0·56, and $_{\mathrm{m}}K$ calc. = $38{\cdot}1 \times 10^{-12}$). However, as Le Fèvre and Le Fèvre[2] failed to detect a significant change in $_{\infty}P_2$ for benzoquinone in carbon tetrachloride with a temperature rise of 29°, and Coop and Sutton[10] clearly demonstrated the temperature-invariance of P_{gas}, we prefer suggestion (*a*).

For chloranil (II), with the angles shown, $b_{\mathrm{L}}^{\mathrm{C-Cl}} = 0{\cdot}32$, and $b_{\mathrm{T}}^{\mathrm{C-Cl}} = b_{\mathrm{V}}^{\mathrm{C-Cl}} = 0{\cdot}22$, the semi-axes forecast are $b_1 = 2{\cdot}222$ (along *OX*), $b_2 = 1{\cdot}889$ (along *OY*), and $b_3 = 1{\cdot}234$. The exaltation (Table 3) is 0·309 unit; this, added to b_1 alone, leads to $_{\mathrm{m}}K$ calc. = $62{\cdot}8 \times 10^{-12}$, or divided equally between b_1 and b_2, to $_{\mathrm{m}}K$ calc. = $51{\cdot}6 \times 10^{-12}$ (observed, $53{\cdot}7 \times 10^{-12}$). Alternatively, it is possible that the C–Cl bonds resemble in anisotropy those in vinylidene chloride[32] (*i.e.*, $b_{\mathrm{L}}^{\mathrm{C-Cl}} = 0{\cdot}399$, $b_{\mathrm{T}}^{\mathrm{C-Cl}} = b_{\mathrm{V}}^{\mathrm{C-Cl}} = 0{\cdot}185$), in which case we have $b_1 = 2{\cdot}216$, $b_2 = 2{\cdot}071$, and $b_3 = 1{\cdot}095$; these, with the exaltation applied to b_1, correspond to a $_{\mathrm{m}}K$ of $80{\cdot}0 \times 10^{-12}$, or, with $\Delta b/2$ added to b_1 and b_2, to a $_{\mathrm{m}}K$ of *ca.* 73×10^{-12}. As with benzoquinone, it seems more reasonable that exaltation should operate most along the conjugated system, and thus supplement b_1. Harmony with experiment can be achieved if (*a*) the anisotropies of the electrostatic and electro-optical polarisabilities are different (for example, if $a_1 = b_1 = 2{\cdot}525$, $a_2 = b_2 = 2{\cdot}071$, $a_3 = 1{\cdot}445$, and $b_3 = 1{\cdot}095$, $_{\mathrm{m}}K$ calc. follows as $53{\cdot}6 \times 10^{-12}$), or (*b*) if a permanent moment resultant acts parallel to b_3 and a_i/b_i is approximately 1·1 as usual (then with $\mu_1 = \mu_2 = 0$, $\mu_3 = 0{\cdot}445$ D, $_{\mathrm{m}}K$ calc. is $53{\cdot}7 \times 10^{-12}$). Unfortunately, no temperature-polarisation data are available for chloranil, and choice between explanations (*a*) or (*b*) must be left open.

The structure reported in ref. 26 for anthraquinone, based on *X*-ray analysis, has C–C–C angles varying irregularly between 116·5° and 122·5°; because this situation may be due to lattice forces, we have retained for (III) as a solute only the value given (117·5°) for C–(CO)–C. The four angles corresponding to h and the twelve corresponding to i (in III) have been taken as 121·25° and 120°, respectively. Computed semi-axes are $b_1 = 2{\cdot}630$, $b_2 = 2{\cdot}582$, and $b_3 = 1{\cdot}416$. Adding the exaltation to b_1 (along *OX*) leads to a predicted $_{\mathrm{m}}K$ of $116{\cdot}6 \times 10^{-12}$; this is about 10% *less* than that found. The discrepancy cannot be remedied by assuming that μ_3 is non-zero, because so doing would further reduce $_{\mathrm{m}}K$ calc.; small alternations of intervalency angles make no significant improvement. An explanation based on non-uniformity of the ratios a_1/b_1, a_2/b_2, and a_3/b_3 again seems most probable, although with this molecule the last ratio cannot exceed the other two without diminution of $_{\mathrm{m}}K$ calc. By illustration, let $a_3/b_3 = 1$, $a_1/b_1 = a_2/b_2 = 1{\cdot}12_{25}$, then $_{\mathrm{m}}K$ calc. would be $130{\cdot}4 \times 10^{-12}$, *i.e.*, the value from experiment. (If preferred, let $a_3/b_3 = 1{\cdot}1$—since we commonly adopt this ratio when $_{\mathrm{D}}P$ and $_{\mathrm{E}}P$ are unknown, believing that often $_{\mathrm{D}}P = 1{\cdot}05R_{\mathrm{D}}$ and $_{\mathrm{E}}P = 0{\cdot}95R_{\mathrm{D}}$—then a_1/b_1 and a_2/b_2 need to be 1·169 to produce the same $_{\mathrm{m}}K$ calc.) By elementary ideas of structure, anthraquinone (III) would be stiffer than benzoquinone and therefore more resistant to those vibrations of the C=O groups required by the Coop–Sutton theory;[10] both the smaller apparent moment, and the signs that atomic polarisation is not excessively developed in the *OZ*-direction, are consistent with this; in contrast, it is difficult to see why orbital distortions[5] should not be the same in molecules (I), (II), and (III).

Regarding naphthaquinone (IV), we have already noted the possibility of a permanent moment by induction (cf. ref. 22) acting in the *OY*-direction. The calculated semi-axes are: $b_1 = 2{\cdot}049$ (along *OX*), $b_2 = 1{\cdot}788$ (along *OY*), and $b_3 = 1{\cdot}012$; to these must be added

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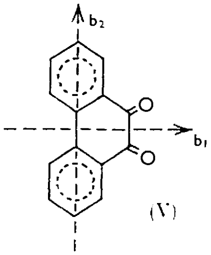
[31] Le Fèvre and Maramba, *J.*, 1952, 235.

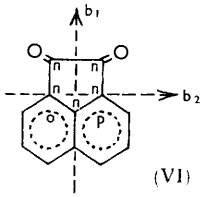
[32] Bramley, Rao, Le Fèvre, and Le Fèvre, *J.*, 1959, 1183.

an observed polarisability exaltation of $\Delta b = 0{\cdot}297$. If Δb wholly supplements b_1, then μ_2 needs to be 1·58 D to produce the ${}_{m}K$ found by experiments; if Δb is divided equally between b_1 and b_2, then a μ_2 of 1·03 D is required. The last estimate is attractive since Hampson and Weissberger[22] give 0·49 D for the moment of 1,4-dichloronaphthalene, and μ(C–Cl) : μ(C=O) is roughly 1 : 2. The "anomalous" part of the apparent moment (1·33 D) of 1,4-naphthaquinone may therefore be of the order of that (Table 2) recorded for anthraquinone (so that minor variations of our assumption that $a_i/b_i = 1{\cdot}1$ are implied; but these are unpredictable).

We turn now to the three quinones of high polarity, phenanthraquinone (V), acenaphthaquinone (VI), and camphorquinone (VII). In (V) let all angles be 120°, leading to $b_1 = 2{\cdot}597$, $b_2 = 2{\cdot}615$, and $b_3 = 1{\cdot}416$; Δb is 0·559, and $\mu_{\text{resultant}}$ is 5·59 D. Adopting $a_i/b_i = 1{\cdot}1$ (for these polar molecules this ratio is unimportant because their molar Kerr constants are predominantly composed of θ_2 terms) and distributing Δb equally over b_1 and b_2, θ_1 and θ_2 become $25{\cdot}7 \times 10^{-35}$ and $591{\cdot}8 \times 10^{-35}$, respectively, and ${}_{m}K$ calc. = 2597×10^{-12} (found, 2570×10^{-12}). Agreement between prediction and measurement is satisfactory.



(V)



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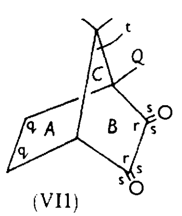

(VII)

In (VI) we assume that the angles marked n are 108°, and those at o and p both 120°; b_1, b_2, and b_3 emerge as 2·531, 2·241, and 1·076, μ_{res} is 6·03 D, and Δb is 0·321. If the exaltation increases b_1, then ${}_{m}K$ calc. is 3150×10^{-12} (compared with 3169×10^{-12} from experiment). Other ways of incorporating Δb in (V) and (VI) produce, of course, different ${}_{m}K$'s; we submit, however, that the allocations made above are reasonable when judged against the structures involved.

Lastly, with camphorquinone (VII), from a " Barton " model we find angles as follow: q = 103°, r = 110°, s = 125°, t = 96°. Planes *A* and *B* intersect mutually at 112°. The C–C bond *Q* lies in plane C. Arbitrary axes of reference are located with *OX* and *OY* in plane *B*, *OX* being parallel to the CO–CO bond; *OZ* is perpendicular to *OX* and *OY*. Calculation by the methods exemplified in refs. 17*b* and 25 then gives principal axes and the direction cosines which define the positions of b_1, b_2, and b_3 in the *OX*, *OY*, *OZ* framework, as shown.

	Direction cosines with			
	X	*Y*	*Z*	
$b_1 = 1{\cdot}832$	0·8539	0·5018	0·1373	$\mu_1 = 2{\cdot}25_3$
$b_2 = 1{\cdot}861$	−0·5200	0·8514	0·0687	$\mu_2 = 3{\cdot}82_3$
$b_3 = 1{\cdot}515$	−0·0230	−0·1525	0·9881	$\mu_3 = 0{\cdot}68_5$

From Table 3 we have $\Delta b = 0{\cdot}309$. Adding this to b_1 (which seems reasonable since conjugation must involve the O=C–C=O unit) makes ${}_{m}K$ calc. = 297×10^{-12}, in satisfactory agreement with 294×10^{-12} observed. If Δb be ignored, ${}_{m}K$ calc. is 372×10^{-12}.

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