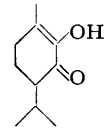
506. *The Dipole Moment and Infra-red Spectrum of Diosphenol.*

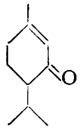
By R. J. W. Le Fèvre, F. Maramba, and R. L. Werner.

The dipole moments and infra-red spectra of diosphenol, piperitone, etc., are examined in relation to the same properties of tropolones.

This note records an examination of diosphenol (I), made as a result of other investigations on enols (cf. Hukins and Le Fèvre, *J.*, 1949, 898; Le Fèvre and Welsh, *J.*, 1949, 1909, 2230; Angyal and Le Fèvre, *J.*, 1950, 562).

(I)





(II)

Experimental

Piperitone (II), having been purified for other work (Le Fèvre and Maramba, *J.*, 1952, 235), was oxidised by 2% potassium permanganate solution as detailed by Penfold (*J. Proc. Roy. Soc. N.S.W.*, 1921, **55**, 139) and the steam-distilled product, after drying, sublimed, giving diosphenol (I) as needles, m. p. 82°, in *ca.* 5% yield. Camphorquinone, required below for comparative purposes, was prepared by selenium dioxide oxidation of the parent ketone (Evans, Ridgion, and Simonsen, *J.*, 1934, 137°).

The infra-red absorption spectra were determined on a Hilger D.209 spectrometer operated as a single-beam instrument with rock-salt prisms and photographic recording or on a Perkin-Elmer instrument, Model 12C, with similar optics and a " Brown " recorder. The frequency calibration was made through the ammonia and atmospheric absorption features catalogued by Oetjen, Kao, and Randall (*Rev. Sci. Instr.*, 1942, **13**, 515) for a sodium chloride prism; the degree of resolution between 5 and 13 μ by both instruments compared satisfactorily with that shown in spectra reproduced in the paper just cited.

Table 1. *Densities and dielectric constants of benzene solutions at 25°.*

$10^6 w_2$	ε^{25}	d_4^{25}	$\alpha\varepsilon_1$	βd_1
0	2·2725	0·87378	—	—
		Diosphenol.		
4,709	2·3014	0·87419	6·14	0·087
7,909	2·3175	0·87459	5·68	0·101
8,567	2·3256	0·87452	6·08	0·098
12,890	2·3474	0·87509	5·81	0·102
13,744	2·3531	0·87509	5·86	0·091
22,969	2·4093	0·87610	5·96	0·101

Whence $\Sigma(\varepsilon_{12} - \varepsilon_1)/\Sigma w_2 = 5·92$, and $\Sigma(d_{12} - d_1)/\Sigma w_2 = 0·097_5$

$10^6 w_2$	ε^{25}	d_4^{25}	$\alpha\varepsilon_1$	βd_1
		Camphorquinone.		
2,321	2·3027	0·87421	13·0	0·185
2,604	2·3068	0·87425	13·2	0·180
8,220	2·3820	0·87518	13·3	0·170
15,485	2·4704	0·87619	12·8	0·156

Whence $\Sigma(\varepsilon_{12} - \varepsilon_1)/\Sigma w_2 = 12·99$, and $\Sigma(d_{12} - d_1)/\Sigma w_2 = 0·164_5$.

Table 2. *Calculation of apparent dipole monents.*

Solute	M_2	$\alpha\varepsilon_1$	β	$_\infty P_2$ (c.c.)	$(R_L)_D$ (c.c.)	μ(D)
Diosphenol	168·2	5·92	0·112	238·2	48·8 *	$3·0_4$
Camphorquinone	166·2	12·99	0·188	452·1	44·3 †	$4·4_6$

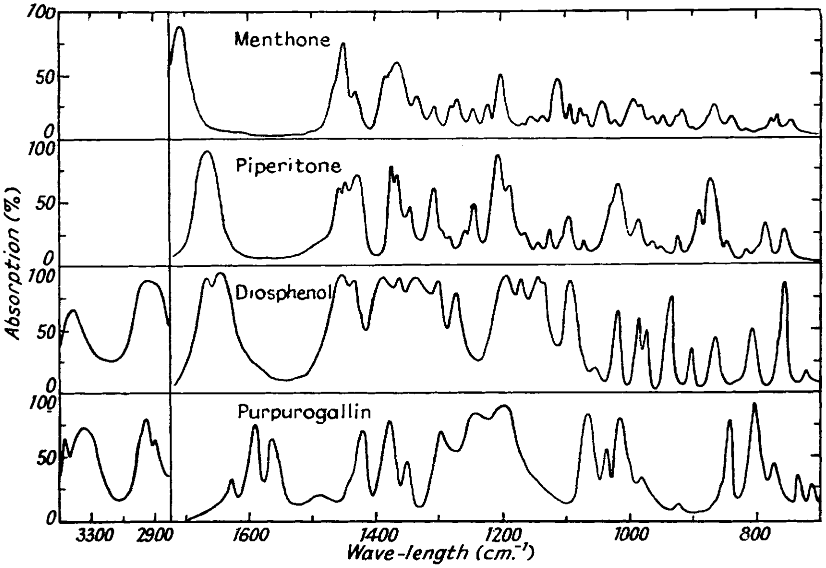
* Observed by von Auwers (*Ber.*, 1924, **57**, 1106).

† Calc. from constants listed by Vogel (*J.*, 1948, 1842).

Table 1 lists the measurements, on solutions in benzene at 25°, which lead to the dipole moments reported in Table 2. Symbols, methods, apparatus, etc., are as described in *Trans. Faraday Soc.*, 1950, **46**, 1, and *J.*, 1948, 1949, except that subscripts 1 and 2 now refer to solvent and solute respectively. This is the reverse of the convention previously followed in these laboratories (cf. *J.*, 1952, 1932).

Discussion.—Guenther (" The Essential Oils," van Nostrand, New York, 1950, Vol. II, p. 542) has summarised past suggestions regarding the correct formulation of diosphenol. The keto–enol structure (I) seems most favoured, although diketo- and dienol variants have been proposed. The last type has been particularly supported more recently by Straneo (*Gazzetta*, 1940, **70**, 27; 1941, **71**, 646).

However, the polarity now found for diosphenol (*viz.*, 3·0—3·1 D) is higher than that to be expected, by analogy, for the dienol: we note that the moment of ethylene glycol is around 2·3 D, while those of the *cis*- and *trans-cyclo*hexane-1 : 2-diol are 2·3 and 2·4 D respectively (Svirbely and Lander, *J. Amer. Chem. Soc.*, 1950, **72**, 3756). Our original intention was to take the moment of camphorquinone (4·5 D) as an estimate of that of the diketo-isomer of (I), but this may not be safe because while the skeleton of a diketo*cyclo*hexane derivative is probably flexible (cf. Le Fèvre and Le Fèvre, *J.*, 1935, 1696; 1938, 494), that of a camphane derivative must be locked. It is relevant that Svirbely and Lander (*loc. cit.*) find both *cyclo*hexane-1 : 2-dione (2·8 D) and 2-hydroxy*cyclo*hexan-1-one (2·9 D) to have moments of the order of that (3·0 D) now given for diosphenol.



The wave-length scale at the left refers to the insets on the two lower curves.

The infra-red spectra are more informative: diosphenol cannot be wholly dienolic as a solid since not only does it absorb intensely at 1668 cm.$^{-1}$, very close to the ketonic frequency at 1666 cm.$^{-1}$ observed with piperitone, but also strongly at 3410 cm.$^{-1}$, *i.e.*, in the region where hydroxyl groups should display themselves. Dissolution of (I) or (II) in benzene or dioxan revealed no notable change with (II): the situation with (I) may be summarised:

Diosphenol	HO bands	C=O bands	C=C bands
Nujol mull	3410 (strong, fairly sharp)	1668	1645 (both strong)
Soln. in dioxan *	3410 (medium, broad)	1669	1646 (1646 stronger)
Soln. in benzene *	3460 (medium, sharp)	1675	1646 (relative strengths as in dioxan, but more so)

* Spectrum not reproduced.

These details have some resemblance to those found by Flett (*J.*, 1948, 1441) for, *e.g.*, 1 : 3-dihydroxyanthraquinone. In general, however, the infra-red spectroscopic evidence supports the representation of diosphenol as (I).

When this work was begun we though that (I) might serve as a guide to the, then unknown, polar and spectral properties of tropolone, since both contain the unit C=C(OH)·CO·C, although in the latter this is further conjugated. Allowing for the last fact by expecting $\mu_{C=O}$ in tropolone to be increased over that in diosphenol as that in piperitone is over that in *cyclo*hexanone (*viz.*, by *ca.* 0·7 D; cf. Le Fèvre and Maramba, *J.*, 1952, 235), we made an upper estimate of μ 3·7—3·8 D for tropolone. Subsequent measurements by Mills and Tyrell (*Chem. and Ind.*, 1951, 30) and Kubo, Nozoe, and Kurita (*Nature*, 1951, **167**, 688) agree with this. Moreover, according to the arguments of Walsh (*Ann. Reports*, 1947, **44**, 45) as μ_{CO} rises so ν_{CO} should fall. Conjugation of C═O and C═C in piperitone lowers ν_{CO} from 1706 cm.$^{-1}$ [now observed for menthone; compare 1714 cm.$^{-1}$ for *cyclo*hexanone (Hartwell, Richards, and Thompson, *J.*, 1948, 1436)] to 1666 cm.$^{-1}$ (see Figure); consequently at the outset we expected ν_{CO} for tropolones to be *ca.* 40 cm.$^{-1}$ lower than for diosphenol.

Purpurogallin (cf. Haworth *et al.*, *J.*, 1950, 1631) was the only tropolone derivative available to us (see Figure, bottom curve); as a solid it exhibited strong absorption at 1590 cm.$^{-1}$ and weaker absorption at 1627 cm.$^{-1}$. Although of lower intensity, the latter seems to be that due to carbonyl.

Since then, the various ν_{CO} reported for simpler tropolones have all lain between 1610 and 1630 cm.$^{-1}$ (Broomfield, *Chem. and Ind.*, 1951, 30; Koch, *J.*, 1951, 512; Haworth and Hobson, *ibid.*, p. 561; Scott and Tarbell, *J. Amer. Chem. Soc.*, 1950, **72**, 240). Such figures are reminiscent of those (1613—1639 cm.$^{-1}$) for *o*-hydroxyacetophenone and the " conjugated chelates " studied by Rasmussen *et al.* (*J. Amer. Chem. Soc.*, 1949, **71**, 1068).

In the ultra-violet region (Beckman spectrophotometer, Model D.U.), our specimens of piperitone and diosphenol gave somewhat broad maxima: piperitone, *ca.* 320 mμ (log ε 1·7), *ca.* 235 mμ (log ε 4·24); diosphenol, *ca.* 273 (log ε 4·05). These are in reasonable accord with others in the literature: piperitone, $\lambda_{max.}$ 3191 (ε 49) (Lowry and Lishmund, *J.*, 1935, 1313) or 3210 Å (ε 54) and 2355, (ε 17,780) (Gillam, Lynas-Gray, Penfold, and Simonsen, *J.*, 1941, 60); diosphenol, $\lambda_{max.}$ 2680 (ε not quoted) (Mayer, *Atti R. Accad. Lincei*, 1914, **23**, 439), 2715 (ε 11,000) (Walker and Read, *J.*, 1934, 230), 2725 (ε 11,150) (Lowry and Lishmund, *loc. cit.*), and 2740 (ε 11,000) (Gillam *et al.*, *loc. cit.*).

Diosphenol therefore differs from tropolone in its ultra-violet absorption since Cook *et al.* (*J.*, 1951, 503) and Haworth and Hobson (*ibid.*, p. 561) find maxima for the latter at two regions, 228 and 237 mμ (log ε, *ca.* 4·4), and 320 and 351 mμ (log ε, *ca.* 3·8).

Acknowledgments are made to U.N.E.S.C.O. for the award of a South East Asian Fellowship to one of us (F. M.) and to the Commonwealth Science Fund for a grant.

UNIVERSITY OF SYDNEY, AND N.S.W. UNIVERSITY OF TECHNOLOGY,
N.S.W., AUSTRALIA.

[*Received, November 10th,* 1953.]