1031. *Molecular Polarisability. The Molar Kerr Constants and Conformations of Citrals and the Corresponding ψ-Ionones as Solutes in Benzene*

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Dipole moments, molar Kerr constants, refractivities, etc., are reported for neral, geranial, and their corresponding ψ-ionones. Comparisons of observed μ's and $_{\mathrm{m}}K$'s with those calculated from bond-moment and polarisability data indicate that these molecules are not likely to exist as all-planar structures. N.m.r. spectra offer little information regarding the preferred conformations, but they do demonstrate that the contributions from isopropenyl types of structure are very small in all cases.

LITTLE information is available regarding the conformations of neral, geranial, and the corresponding ψ-ionones. Past work on citrals and many other terpene derivatives has been mainly concerned with the position of the terminal C=C bond. Much of the older chemical evidence[1] was ambiguous and suggested that these substances existed as

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[1] J. L. Simonsen and L. N. Owen, "The Terpenes," Cambridge University Press, Cambridge, 2nd edn., vol. 1, 1953, p. 88.

mixtures containing both isopropenyl and isopropylidene end-groupings. By contrast, physical methods (ultraviolet [2] and infrared spectroscopy,[3] and *X*-ray diffraction [4,5]) indicated structural homogeneity, and favoured the $Me_2C=CH^-$ arrangement. The recently recorded nuclear magnetic resonance (n.m.r.) spectra of citrals [6] and ψ-ionones [7] show that, if mixtures occur at all, the proportions of molecules with isopropenyl groups must be very small. The measurements reported below were started in the hope that the anisotropic polarisabilities of the C=C and C=O bonds would make possible the deduction, at least, of the mutual inclinations of these links in structures containing both of them.

EXPERIMENTAL

Solutes, Methods, etc.—Commercial natural citral was distilled, the fraction with b. p. 97°/17 mm., n_D^{25} 1·4850, being collected for measurement. Part of this material (estimated from its n.m.r. spectrum to contain about 40% of neral) was then converted, *via* the normal bisulphite addition compound [8] and subsequent decomposition by aqueous sodium hydrogen carbonate, into crude geranial, from which, by redistillation, the aldehyde was obtained (b. p. 84—85°/2 mm., n_D^{25} 1·4875; 2,4-dinitrophenylhydrazone, m. p. 134·5°; infrared spectrum identical with that of an authentic sample [9]). The condensation of geranial and acetone (cf. ref. 10) provided α-ψ-ionone (b. p. 122—123°/2·6 mm., n_D^{25} 1·5302; infrared spectrum showing a characteristic triplet [11] between 1570 and 1700 cm.$^{-1}$). Mixtures of ψ-ionones were formed from natural citral and acetone; the sample used for the measurements in Table 1 had b. p. 136—138°/3 mm., n_D^{25} 1·5253. Purification through the bisulphite addition product [10] provided a satisfactory alternative route to the pure α-ketone.

Details of apparatus, procedures, symbols, etc., have been given before.[12] The n.m.r. spectra were taken on a Varian A-60 spectrometer, operating at 35°; solutions used contained 5—10% (w/v) of solutes in deuteriochloroform with tetramethylsilane as internal reference.

Measurements and Results.—These follow, under the usual headings,[12] as Tables 1 and 2. The equations used in passing from Table 1 to Table 2 have been given previously.[13]

No previous data on the dipole moments and the electric double refractions of these carbonyl compounds can be found in the literature.

N.m.r. Spectra.—The n.m.r. spectra recorded here for the citrals are in good agreement with those published by Venuto and Day,[6] although for geranial (citral a) the doublet due to the aldehydic proton has a separation of 8·4 instead of the 7·8 c./sec. reported.[6] The spectrum of the geranial described above indicates that it is contaminated with *ca.* 10—15% of neral (citral b). However, since such samples show the same dipole moment, molar refraction, and molar Kerr constant as commercial natural citral containing about 40% of neral, it is not unreasonable to assume that geranial and neral have the same polarity and polarisability.

The n.m.r. spectrum of α-ψ-ionone shows a doublet at $\tau = 8{\cdot}36$ p.p.m. ($J = 4{\cdot}5$ c./sec.; isopropylidene methyls), a singlet at 8·09 ($CO{\cdot}CH_3$), a strong group of lines near 7·80 (four allylic CH_2 protons, with the methyl protons from $CMe{:}CH{\cdot}CH{:}C$ superimposed), an unresolved multiplet at 4·90 (olefinic proton in the isopropylidene unit), a broad doublet centred at 3·98 ($J = 12{\cdot}5$ c./sec.; $CMe{:}CH{\cdot}CH{:}C$), a fairly sharp doublet centred at 3·93 ($J = 15{\cdot}5$ c./sec.;

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[2] R. Kuhn and H. Roth, *Ber.*, 1932, **65**, 1285.

[3] D. Barnard, L. Bateman, A. J. Harding, H. P. Koch, N. Sheppard, and G. B. B. M. Sutherland, *J.*, 1950, 915.

[4] L. Bateman and G. A. Jeffrey, *Nature*, 1943, **152**, 446.

[5] G. A. Jeffrey, *Proc. Roy. Soc.*, 1945, *A*, **183**, 388.

[6] P. B. Venuto and A. R. Day, *J. Org. Chem.*, 1964, **29**, 2735.

[7] Present Paper.

[8] (*a*) F. Tiemann, *Ber.*, 1899, **32**, 115; (*b*) H. Hibbert and L. T. Cannon, *J. Amer. Chem. Soc.*, 1924, **46**, 119.

[9] Y.-R. Naves, *Bull. Soc. chim. France*, 1952, 522.

[10] *Org. Synth.*, 1955, **3**, 747.

[11] N. A. Slovokhotova, G. I. Samokhvalor, G. M. Kunitskaya, and M. A. Micropol'skaya, *Zhur. obshchei Khim.*, 1954, **24**, 2222.

[12] C. G. Le Fèvre and R. J. W. Le Fèvre, (*a*) *Rev. Pure Appl. Chem.* (*Australia*), 1955, **5**, 261; (*b*) Ch. XXXVI in " Physical Methods of Organic Chemistry," ed. Weissberger, Interscience, New York, 3rd edn., 1960, vol. 1, p. 2459.

[13] R. J. W. Le Fèvre and K. M. S. Sundaram, *J.*, 1962, 1494.

:C*H*·COMe), and a pseudo-quartet centred at 2·58 (C:CH·C*H*:H·COMe); fine structures observed are probably due to virtual or long-range coupling of the proton at $\tau = 3{\cdot}98$ p.p.m.[15] The spectrum of the mixture of ψ-ionones is very similar to that of α-ψ-ionone except that there is a more complicated splitting pattern around $\tau = 7{\cdot}45$ p.p.m. (resembling the change from citral a to citral b), and most of the signals at lower field are broadened. No signal can

TABLE 1

Incremental Kerr effects, refractive indices, dielectric constants, and densities for solutions containing weight fractions w_2 of solute in benzene * at 25°

Natural citral

$10^5 w_2$	237	540	575	824	851	909	1099	1137	1192	1267	1785
$10^{11}\Delta B$	881	1836	1928	2882	3161	3337	3796	4165	4149	4426	—
$10^4\Delta\varepsilon$	241	543	—	836	—	—	1116	—	—	1266	1814

$10^5 w_2$	620	1142	1881	2430
$10^4\Delta d$	—	—	1	2
$10^4\Delta d$	1	2	2	3

whence $\Sigma\Delta B/\Sigma w_2 = 35{\cdot}41 \times 10^{-7}$; $\Sigma\Delta\varepsilon/\Sigma w_2 = 10{\cdot}15$; $\Sigma\Delta d/\Sigma w_2 = 0{\cdot}0077$; $\Sigma\Delta n/\Sigma w_2 = -0{\cdot}012$; $\Sigma\Delta n^2/\Sigma w_2 = -0{\cdot}036$.

Geranial

$10^5 w_2$	479	576	649	793	961	1088
$10^{11}\Delta B$	1744	2062	2281	2636	3451	3740
$10^4\Delta\varepsilon$	479	583	661	799	969	1110

$10^5 w_2$	1921	3015	4527
$10^4\Delta d$	1	2	4
$-10^4\Delta n$	2	2	5

whence $\Sigma\Delta B/\Sigma w_2 = 35{\cdot}00 \times 10^{-7}$; $\Sigma\Delta\varepsilon/\Sigma w_2 = 10{\cdot}12$; $\Sigma\Delta d/\Sigma w_2 = 0{\cdot}0074$, $\Sigma\Delta n/\Sigma w_2 = -0{\cdot}012$; $\Sigma\Delta n^2/\Sigma w_2 = -0{\cdot}0345$.

α-ψ-Ionone

$10^5 w_2$	218	372	482	522	560	709
$10^{11}\Delta B$	910	—	1982	2325	2354	2996
$10^4\Delta\varepsilon$	174	300	384	426	452	572

$10^5 w_2$	1682	2581	3217	709
$10^4 d$	2	4	5	1
$10^4 n$	5	9	12	2

whence $\Sigma\Delta B/\Sigma w_2 = 42{\cdot}42 \times 10^{-7}$; $\Sigma\Delta\varepsilon/\Sigma w_2 = 8{\cdot}06$; $\Sigma\Delta d/\Sigma w_2 = 0{\cdot}0195$; $\Sigma\Delta n/\Sigma w_2 = 0{\cdot}033$; $\Sigma\Delta n^2/\Sigma w_2 = 0{\cdot}099$.

Mixture of ψ-ionones

$10^5 w_2$	485	540	612	963	1100	2259
$10^{11}\Delta B$	2036	2255	2751	3946	—	—
$10^4\Delta\varepsilon$	361	388	441	705	817	1684
$10^4\Delta d$	—	2	—	3	4	8
$10^4\Delta n$	—	1	—	2	3	6

whence $\Sigma\Delta B/\Sigma w_2 = 42{\cdot}26 \times 10^{7}$; $\Sigma\Delta\varepsilon/\Sigma w_2 = 7{\cdot}38$; $\Sigma\Delta d/\Sigma w_2 = 0{\cdot}0350$; $\Sigma\Delta n/\Sigma w_2 = 0{\cdot}0247$; $\Sigma\Delta n^2/\Sigma w_2 = 0{\cdot}0741$.

* When $w_2 = 0$, $B_1 = 0{\cdot}410 \times 10^{-7}$, $\varepsilon = 2{\cdot}2725$, $d_1 = 0{\cdot}8738$, and $n_1 = 1{\cdot}4973$.

TABLE 2

Polarisations, molar Kerr constants, dipole moments, etc., calculated from Table 1

Solute	$\alpha\varepsilon_1$	β	γ	δ	$10^{12}\ {}_\infty({}_mK_2)$	P_2 (c.c.)	R_D (c.c.)	ΔR_D (c.c.) *	μ (D) †
Natural citral	10·15	0·009	−0·008	86·37	950·0	342·17	49·50	1·97	3·76
Geranial	10·12	0·009	−0·008	85·37	940·0	341·32	49·57	2·03	3·76
α-ψ-Ionone ...	8·06	0·012	0·012	103·46	1463·0	355·60	66·77	5·59	3·74
Mixture of ψ-ionones	7·38	0·0400	0·016	103·07	1461·6	329·84	64·56	3·38	3·58

* $\Delta R_D = R_D$ (obs.) − R_D (calc.) from bond refractions of Vogel *et al.*[14] † Calculated by assuming ${}_DP = 1{\cdot}05\ R_D$.

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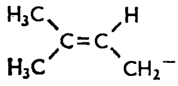
[14] A. I. Vogel, W. T. Cresswell, G. H. Jeffery, and J. Leicester, *J.*, 1952, 514.

[15] (*a*) J. I. Musher and E. J. Corey, *Tetrahedron*, 1962, **18**, 791; (*b*) N. S. Bhacca and D. H. Williams, " Application of N.M.R. Spectroscopy in Organic Chemistry," Holden-Day, San Francisco, 1964, ch. 5.

be found around $\tau = 5{\cdot}34$ for the samples studied; therefore [16a] the proportions of isopropenyl types of structure in the citrals or the ψ-ionones, if any, cannot be significant.

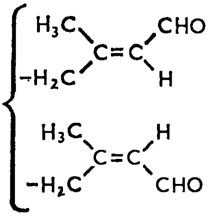
DISCUSSION

Molecular Conformations of Citrals.—Judging from their structures, the isomers of citral can be regarded as consisting of two planar portions (Ia,Ib, and Ia,Ic), and therefore the conformations may be conveniently considered by treating these two portions separately and then rejoining them. As for the isopropylidene part (Ia), we have, from the usual bond data [17] and after maximisation,[18] the semi-axes * shown below diagram (A). For the polar groups, (Ib) and (Ic), since the resultant moments of the molecules are both 3·76 D and the " exaltations " both *ca.* 2·03 c.c., the *s-trans* configurations [19] are clearly appropriate. Calculation of the principal axes, after the exaltation has been added to the C=O direction, gives the results shown below (B). Thus, b_1' makes an angle of less than 5° with the x'-axis; this implies that the two isomeric forms of citral should have the same dipole moments and molar Kerr constants. Accordingly, we cannot expect to distinguish between them by polarisation and polarisability measurements.



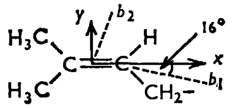
(Ia)

and



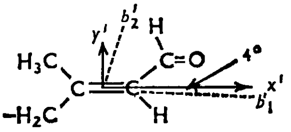
(Ib) for geranial

(Ic) for neral



(A)

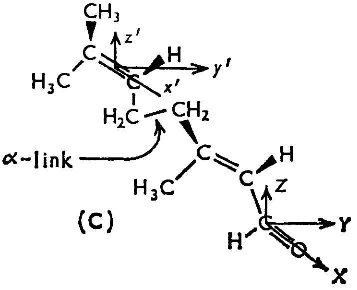
$b_1 = 10{\cdot}01,\ b_2 = 8{\cdot}82,\ b_3 = 7{\cdot}34$



(B)

$b_1' = 13{\cdot}25,\ b_2' = 9{\cdot}03,\ b_3' = 6{\cdot}52$

α = the angle between Z- and x'-axes;
β = the angle between XY- and $x'y'$-planes;
γ = the angle which the projection of the α-link on the XY-plane makes with the positive Z-axis in a counter-clockwise direction.



(C)

In putting the two parts together, the all-planar form (in which x_1 is parallel to x_1', y_2 to y_2', and z_3 to z_3') was considered first; this gave a calculated molar Kerr constant of

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* Here and elsewhere polarisabilities are expressed as 10^{-24} c.c. units.

[16] L. M. Jackman, " Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, New York, 1959, (*a*) p. 61; (*b*) p. 85.

[17] R. J. W. Le Fèvre, *J. Proc. Roy. Soc. New South Wales*, 1961, **95**, 1

[18] J. M. Eckert and R. J. W. Le Fèvre, *J.*, 1962, 1081.

[19] C.-Y. Chen and R. J. W. Le Fèvre, *J.*, 1964, 234.

1283×10^{-12} (assuming as before[19] that the resultant moment acts in the C=O direction). Such a high value in comparison with the experimental one of 950×10^{-12} indicates strongly that the citrals do not have all-flat conformations. If now we twist the isopropylidene unit around and define three angles α, β, and γ, as in diagram (C), it is found that for the following sets of angles (measured from Barton scale models): (a) $\alpha = 20°$, $\beta = 60°$, $\gamma = 20°$; (b) $\alpha = 25°$, $\beta = 65°$, $\gamma = 18°$; (c) $\alpha = 30°$, $\beta = 70°$, $\gamma = 13°$; (d) $\alpha = 27°$, $\beta = 68°$, $\gamma = 16°$, calculated molar Kerr constants emerge as tabulated below.

		Direction cosines with			
	$10^{24}b$ (calc.)	X	Y	Z	$10^{12}(_{\mathrm{m}}K_2)$ (calc.)
Set (a)	$b_1 = 22{\cdot}65$	0·992	0·118	0·035	
	$b_2 = 18{\cdot}24$	−0·117	0·823	0·555	895·8
	$b_3 = 15{\cdot}61$	0·037	−0·555	0·831	
Set (*b*)	$b_1 = 22{\cdot}78$	0·992	0·115	0·048	
	$b_2 = 17{\cdot}92$	−0·121	0·799	0·589	923·6
	$b_3 = 15{\cdot}81$	0·029	−0·590	0·807	
Set (c)	$b_1 = 22{\cdot}91$	0·993	0·103	0·061	
	$b_2 = 17{\cdot}61$	−0·119	0·778	0·617	953·0
	$b_3 = 15{\cdot}99$	0·016	−0·620	0·784	
Set (d)	$b_1 = 22{\cdot}83$	0·994	0·104	0·041	
	$b_2 = 17{\cdot}69$	−0·107	0·789	0·606	940·0
	$b_3 = 15{\cdot}97$	0·030	−0·606	0·795	

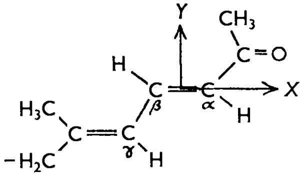
To judge from the observed and calculated molar Kerr constants, the conformation defined by set (d) may well be one of the preferred conformations for the citrals, although it may not occur uniquely. The assignment of such a semi-cyclic structure seems to be reconcilable with the following chemical evidence. (i) Nerol, the alcohol from neral, can be cyclised to α-terpineol by dilute sulphuric acid nine times faster than the corresponding geraniol in which the reacting centres are farther apart. (ii) The more sterically hindered neral is not attacked by cyanoacetate. (iii) The normal bisulphite addition product of the less hindered geranial is hydrolysable by sodium carbonate, which has no effect on the adduct of neral.

Molecular Conformations of ψ-Ionones.—From Table 2 it is seen that, although the mixture of ψ-ionones exhibits total polarisations and molar refractions which differ slightly from those of α-ψ-ionone, the molar Kerr constants of these two preparations are the same. However, observational inaccuracies are not thereby necessarily implied, since total polarisations and molar refractions depend upon the measured quantities $\alpha\varepsilon_1$, β, and γ, while molar Kerr constants in cases such as the present, when $_{\mathrm{m}}K$ is large, are overwhelmingly determined by δ, and the numerical effects of $\alpha\varepsilon$, β, and γ are insignificant. There is no reason to suppose that small amounts of impurities will sensitively alter $\alpha\varepsilon$, β, γ, and δ proportionately. Accepting, therefore, that the $_{\mathrm{m}}K$'s of α- and β-ψ-ionone are identical, we can regard the ψ-ionones as composed of two planar units, namely, (Ia) and the remaining polar section.

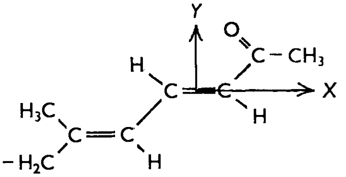
In the case of α-ψ-ionone, the latter may have the possible conformations (IIa), (IIb), (III), and (IV) (in which the designations *trans* and *cis* relate to the $C{:}C{\cdot}C{:}O$ double bonds). However, a coupling constant of 15·5 c./sec. between the α- and the β-protons and one of 12·5 c./sec. between the β- and the γ-protons suggests[16b] that all these protons are *trans* to one another; thus the conformations (III) and (IV) are disfavoured, and therefore only the first two cases need be considered.

Assuming that the polar portion of α-ψ-ionone exists in conformation (IIa), with an " exaltation " (an estimation) of 7 c.c acting along the x-axis direction, we have $b_{xx} = 25{\cdot}51$, $b_{yy} = 13{\cdot}95$, $b_{zz} = 10{\cdot}31$, $b_{xy} = 0{\cdot}31$, and $b_{xz} = b_{yz} = 0$. Alternatively, if the polar portion has the conformation (IIb), the corresponding sets of semi-axes are $b_{xx} = 27{\cdot}76$, $b_{yy} = 25{\cdot}74$, $b_{zz} = 20{\cdot}48$, $b_{xy} = 0{\cdot}265$, $b_{xz} = 0{\cdot}170$, and $b_{yz} = 0{\cdot}850$, with an assumed " exaltation " of 4 c.c. being applied along the (Acetyl)–(C_α) link.

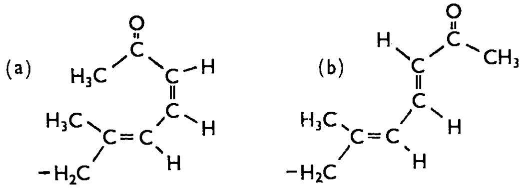
In joining the non-polar (Ia) and the polar parts (IIa or b) together, we have to assume further that the spatial disposition of the isopropene group remains the same as that in the citrals; based on this premise and predicted dipole moments of 4·2 and 3·2 D, respectively, for (IIa) and (IIb), we obtain:



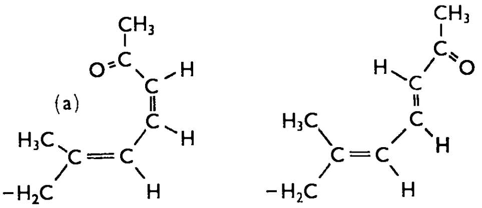
(IIa) *trans* and *trans*



(IIb) *trans* and *cis*



(III) *cis* and *trans*



(IV) *cis* and *cis*

b_i (calc.)	Direction cosines with X	Y	Z	$10^{12}{}_{\mathrm{m}}K_2$ (calc.)
	for the *trans,trans*-form (IIa)			
$b_1 = 35{\cdot}08$	0·998	0·067	0·016	
$b_2 = 22{\cdot}34$	−0·068	0·910	0·410	2775·4
$b_3 = 20{\cdot}10$	0·014	−0·410	0·912	
	for the *trans-cis*-form (IIb)			
$b_1 = 29{\cdot}63$	0·817	0·572	0·068	
$b_2 = 24{\cdot}02$	−0·575	0·861	0·165	−88·2
$b_3 = 20{\cdot}34$	0·040	−0·410	0·984	

By comparing the above results with the experimental molar Kerr constant (1463 × 10^{-12}), we may infer that α-ψ-ionone, as a solute in benzene, exists as a mixture containing 55% of the conformer (IIa) and 45% of (IIb). As for β-ψ-ionone, if this has the same molar Kerr constant as α-ψ-ionone, it can be viewed as a mixture of 45% *trans,trans*- and 55% *trans,cis*-conformations. The molar Kerr constants calculated for these two conformers then follow as 2775·4 and 518·0 × 10^{-12}, respectively.

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