38. *Molecular Polarisability: The Molar Kerr Constants and Conformations of Acrylic, Crotonic, Methacrylic, and Tiglic Aldehydes, as Solutes in Benzene.*

By C.-Y. CHEN and R. J. W. LE FÈVRE.

For the aldehydes named above, molar Kerr constants ($\times 10^{12}$) at infinite dilution in benzene are reported as 385, 738, 299, and 716, respectively. By reference to anisotropic bond polarisabilities, redetermined dipole moments, molecular refractions, etc., the ${}_{\mathrm{m}}K$'s and μ's can be reconciled if the solutes exist at 25° as *s-trans–s-cis* mixtures as follow: $\mathrm{CH_2{:}CH{\cdot}CHO}$ 4 : 1, $\mathrm{Me{\cdot}CH{:}CH{\cdot}CHO}$, 23 : 1, $\mathrm{CH_2{:}CMe{\cdot}CHO}$, 1 : 1, and $\mathrm{Me{\cdot}CH{:}CMe{\cdot}CHO}$, 18 : 1.

PREDICTED and observed dipole moments (D) for the four aldehydes named in the title were given by Bentley, Everard, Marsden, and Sutton [1] as:

	s-cis	*s-trans*	obs.
$\mathrm{CH_2{:}CH{\cdot}CHO}$	2·44	2·78	2·90 (in benzene [1])
$\mathrm{Me{\cdot}CH{:}CH{\cdot}CHO}$	2·74	3·45	3·54 (in $\mathrm{CCl_4}$ [1])
$\mathrm{CH_2{:}CMe{\cdot}CHO}$	2·85	2·38	2·72 (in benzene [2])
$\mathrm{Me{\cdot}CH{:}CMe{\cdot}CHO}$	3·10	3·09	3·39 (,,)

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[1] Bentley, Everard, Marsden, and Sutton, *J.*, 1949, 2957.

[2] Rogers, *J. Amer. Chem. Soc.*, 1947, **69**, 1243.

Thus from polarity considerations they concluded " that acraldehyde and crotonaldehyde adopt the *s-trans*-configuration, but that it is impossible to say with certainty that methacraldehyde and tiglaldehyde do so."

Since such rotational isomers should differ in their anisotropies of polarisability we calculated the molar Kerr constants to be expected for the *s-cis-* and the *s-trans*-extremes and found them to be separated sufficiently in each case to justify comparison with direct measurements.

EXPERIMENTAL

Solutes, Methods, etc.—Commercial acraldehyde (from B.D.H.) was dried ($MgSO_4$) and distilled through a short column; the fraction of b. p. 53°/765 mm. was collected for measurement. Crotonaldehyde (also from B.D.H.), after similarly drying and fractionation under nitrogen, had b. p. 102°/762 mm. and n_D^{25} 1·4348. Methacraldehyde was synthesised as described by Marrel, Myers, and Sanders,[3] refluxing being continued for 4 hr.; the specimen used had b. p. 66·2—66·8°/752 mm. and n_D^{25} 1·4053. Tiglaldehyde was prepared as directed by Green and Hickinbottom;[4] successive fractionations (in a nitrogen atmosphere) provided material with b. p. 118·5—119·5°/760 mm. and n_D^{25} 1·4437.

Details of apparatus, procedures, symbols, etc. have been given before.[5]

TABLE 1.

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

Solute: Acraldehyde

$10^5 w_2$	380	517	827	1069	1250	1516
$10^{11}\Delta B$	1532	2056	3363	4379	4898	5895

whence $\Sigma\Delta B/\Sigma w_2 = 39{\cdot}80 \times 10^{-7}$.

Solute: Crotonaldehyde

$10^5 w_2$	158	279	301	384	504	526	633	724	932
$10^{11}\Delta B$	932	1629	1880	2301	—	3083	3820	4477	5581
$10^4\Delta\varepsilon$	—	508	—	697	910	968	1168	1314	1720
$-10^4\Delta d$	—	1	—	1	1	2	2	2	3
$10^5 w_2$	386	761	1180	1572	3205				
$-10^4\Delta n$	1	2	4	10	21				

whence $\Sigma\Delta B/\Sigma w_2 = 60{\cdot}21 \times 10^{-7}$, $\Sigma\Delta\varepsilon/\Sigma w_2 = 18{\cdot}30$, $\Sigma\Delta d/\Sigma w_2 = -0{\cdot}030$, $\Sigma\Delta n/\Sigma w_2 = -0{\cdot}054$, and $\Sigma\Delta n^2/\Sigma w_2 = -0{\cdot}162$.

Solute: Methacraldehyde

$10^5 w_2$	138	333	521	943	2067
$10^{11}\Delta B$	348	814	1293	2361	—
$10^4\Delta\varepsilon$	154	375	584	1066	2351
$-10^4\Delta d$	—	1	2	4	9
$-10^4\Delta n$	—	2	4	6	—

whence $\Sigma\Delta B/\Sigma w_2 = 24{\cdot}89 \times 10^{-7}$, $\Sigma\Delta\varepsilon/\Sigma w_2 = 11{\cdot}32$, $\Sigma\Delta d/\Sigma w_2 = -0{\cdot}041$, $\Sigma\Delta n/\Sigma w_2 = -0{\cdot}067$, and $\Sigma\Delta n^2/\Sigma w_2 = -0{\cdot}201$.

Solute: Tiglaldehyde

$10^5 w_2$	234	277	330	424	491	644	1028
$10^{11}\Delta B$	1048	1306	1574	2142	2544	3047	—
$10^4\Delta\varepsilon$	331	—	491	652	735	945	1493
$-10^4\Delta d$	—	—	—	—	—	1	2
$10^5 w_2$	650	971	1940	2300			
$-10^4\Delta n$	3	4	7	8			

whence $\Sigma\Delta B/\Sigma w_2 = 48{\cdot}59 \times 10^{-7}$, $\Sigma\Delta\varepsilon/\Sigma w_2 = 14{\cdot}74$, $\Sigma\Delta d/\Sigma w_2 = -0{\cdot}018$, $\Sigma\Delta n/\text{-}w_2 = -0{\cdot}04$, and $\Sigma\Delta n^2/\Sigma w_2 = -0{\cdot}12$.

* When $w_2 = 0$, $B_1 = 0{\cdot}410 \times 10^{-7}$, $\varepsilon_1 = 2{\cdot}2725$, $d_1 = 0{\cdot}8738$, $n_1 = 1{\cdot}4973$.

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[3] Marrel, Myers, and Sanders, *J. Amer. Chem. Soc.*, 1948, **70**, 1697.

[4] Green and Hickinbottom, *J.*, 1957, 3267.

[5] Le Fèvre and Le Fèvre, (*a*) *Rev. Pure Appl. Chem.*, 1955, **5**, 261; (*b*) Ch. XXXVI in " Physical Methods of Organic Chemistry," ed. Weissberger, Interscience Publ. Inc., New York, 3rd edn., Vol. I, p. 2459.

Measurements and Results.—These follow under the usual headings[5] as Tables 1 and 2. Equations used in passing from Table 1 to Table 2 have recently been summarised.[6]

TABLE 2.

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

Solute	$\alpha\varepsilon_1$	$-\beta$	$-\gamma$	δ	$10^{12}{}_{\infty}({}_{m}K_2)$
Acraldehyde	15·80 *	0·066 *	$0{\cdot}069_5$ *	97·07	385·1
Crotonaldehyde	18·30	0·034	0·036	$146{\cdot}8_5$	738·1
Methacraldehyde	11·32	0·047	0·045	60·70	299·4
Tiglaldehyde	14·74	0·021	0·033	118·5	715·8

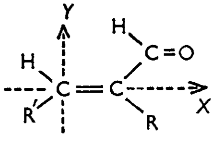
Solute	${}_{\infty}P_2$ (c.c.)	R_D (c.c.)	ΔR_D (c.c.) †	μ (D) ‡
Acraldehyde	187·0	16·69	1·20	2·88
Crotonaldehyde	266·0	22·28	2·14	3·44
Methacraldehyde	174·2	21·91	1·77	2·72
Tiglaldehyde	262·5	26·96	2·19	3·38

* Calc. from data in ref. 1. † $\Delta R_D = R_D$ observed *minus* R_D calc. from bond refractions of Vogel *et al.*[8] ‡ Calc. by assuming ${}_{D}P = 1{\cdot}05R_D$.

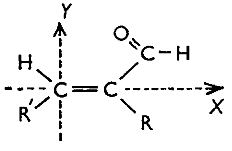
The dipole moments now found confirm those recorded in refs. 1 and 2; the fact that for crotonaldehyde μ appears to be 0·1 D lower in benzene than in carbon tetrachloride is reasonably explicable as due to solvent effects.[7] No previous data on the electric double refractions of these aldehydes can be found in the literature.

DISCUSSION

Prediction of Molar Kerr Constants of s-cis- *and* s-trans-*Conformations of Structures of type* CHR′:CR·CHO.—Calculations proceed by two stages: (*a*) deduction of the principal semi-axes of the molecular polarisability ellipsoids for species (I) and (II), and (*b*) evaluation of the appropriate molar Kerr constants therefrom. Through lack of information, certain assumptions must be made. We take the CCC and CCO angles in the four aldehydes to be as reported[9] in acraldehyde and crotonaldehyde, *viz.*, 120°, and use bond polarisabilities as listed in ref. 10 for C–H, C–C, C=C, and C=O. Exaltations of polarisability (evaluated as $9\Delta_E P/4\pi N$, with $\Delta_E P$ taken as $0{\cdot}95\Delta R_D$, from Table 2) are applied along the C=C or C=O axes in the *s-trans*-forms, and along the C–(CO) axes in the *s-cis*-forms (these directions being probably close to those of the conjugative displacements in the two conformations; cf. ref. 5*a*, p. 301). Results of computations for stage (*a*) are summarised in Table 3. Principal axes b_1, b_2, and b_3 (in 10^{-23} c.c.) are located in (I) or (II) by reference to the arbitrary axes X, Y, and Z, the first two of which are in the molecular planes, as shown (such calculations are briefly outlined in ref. 5*b*, p. 2486, more fully in ref. 11). Molar Kerr constants predicted at stage (*b*) are given in Table 4; these depend, of course, on the dipole moments assumed for the pure species (I) and (II).



(I) s-trans



(II) s-cis

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

[7] Le Fèvre, " Dipole Moments," Methuen, London, 3rd edn., 1953, Ch. III.

[8] Vogel, Cresswell, Jeffrey, and Leicester, *J.*, 1952, 514.

[9] " Tables of Interatomic Distances and Configuration in Molecules and Ions," Sutton *et al.*, *Chem. Soc. Spec. Publ.* No. 11, 1958, M 147 and 166.

[10] Le Fèvre, Liversidge Lecture, *J. Proc. Roy. Soc. New South Wales*, 1961, **95**, 1.

[11] Eckert and Le Fèvre, *J.*, 1962, 1081.

TABLE 3.

Polarisability semi-axes and their locations.

Semi-axes	Direction cosines with X	Y	Z	Semi-axes	Direction cosines with X	Y	Z
	s-trans-isomer				*s-cis*-isomer		
			Acraldehyde, $\Delta b = 0{\cdot}136$				
$b_1 = 0{\cdot}949$	$+0{\cdot}996$	$-0{\cdot}100$	0	$b_1 = 0{\cdot}790$	$+0{\cdot}922$	$-0{\cdot}387$	0
$b_2 = 0{\cdot}549$	$+0{\cdot}100$	$+0{\cdot}996$	0	$b_2 = 0{\cdot}710$	$+0{\cdot}387$	$+0{\cdot}922$	0
$b_3 = 0{\cdot}406$	0	0	1	$b_3 = 0{\cdot}406$	0	0	1
			Crotonaldehyde, $\Delta b = 0{\cdot}242$				
$b_1 = 1{\cdot}233$	$+0{\cdot}992$	$-0{\cdot}129$	0	$b_1 = 0{\cdot}862$	$+0{\cdot}751$	$-0{\cdot}660$	0
$b_2 = 0{\cdot}752$	$+0{\cdot}129$	$+0{\cdot}992$	0	$b_2 = 1{\cdot}124$	$+0{\cdot}660$	$+0{\cdot}751$	0
$b_3 = 0{\cdot}561$	0	0	1	$b_3 = 0{\cdot}561$	0	0	1
			Methacraldehyde, $\Delta b = 0{\cdot}200$				
$b_1 = 1{\cdot}183$	1	0	0	$b_1 = 1{\cdot}021$	$+0{\cdot}750$	$-0{\cdot}661$	0
$b_2 = 0{\cdot}760$	0	1	0	$b_2 = 0{\cdot}925$	$+0{\cdot}661$	$+0{\cdot}750$	0
$b_3 = 0{\cdot}561$	0	0	1	$b_3 = 0{\cdot}561$	0	0	1
			Tiglaldehyde, $\Delta b = 0{\cdot}247$				
$b_1 = 1{\cdot}407$	$+0{\cdot}997$	$+0{\cdot}077$	0	$b_1 = 1{\cdot}294$	$0{\cdot}817$	$-0{\cdot}576$	0
$b_2 = 0{\cdot}968$	$-0{\cdot}077$	$+0{\cdot}997$	0	$b_2 = 1{\cdot}083$	$0{\cdot}576$	$0{\cdot}817$	0
$b_3 = 0{\cdot}716$	0	0	1	$b_3 = 0{\cdot}716$	0	0	1

TABLE 4.

Moment components * and predicted molar Kerr constants.

Assumed μ (*s-trans*)	Moment components	$10^{12}{}_{\mathrm{m}}K$ (calc.)	Assumed μ (*s-cis*)	Moment components	$10^{12}{}_{\mathrm{m}}K$ (calc.)
		Acraldehyde, $_\infty({}_{\mathrm{m}}K_2) = 385$			
2·78	$\mu_1 = +2{\cdot}77, \mu_2 = +0{\cdot}28$	+393	2·44	$\mu_1 = -1{\cdot}94, \mu_2 = +1{\cdot}48$	+119
2·90	$\mu_1 = +2{\cdot}89, \mu_2 = +0{\cdot}29$	+449	2·56	$\mu_1 = -2{\cdot}04, \mu_2 = +1{\cdot}55$	+142
		Crotonaldehyde, $_\infty({}_{\mathrm{m}}K_2) = 738 \times 10^{-12}$			
3·45	$\mu_1 = +3{\cdot}41, \mu_2 = +0{\cdot}44$	+768	2·74	$\mu_1 = -2{\cdot}595, \mu_2 = +0{\cdot}878$	+61·0
		Methacraldehyde, $_\infty({}_{\mathrm{m}}K_2) = 299$			
2·38	$\mu_1 = +2{\cdot}38, \mu_2 = 0$	+342	2·85	$\mu_1 = -2{\cdot}7001, \mu_2 = +0{\cdot}9116$	+244·5
		Tiglaldehyde, $_\infty({}_{\mathrm{m}}K_2) = 716 \times 10^{-12}$			
3·09	$\mu_1 = +3{\cdot}08, \mu_2 = -0{\cdot}24$	+614	3·10	$\mu_1 = -2{\cdot}81, \mu_2 = +1{\cdot}30$	+372
3·38	$\mu_1 = +3{\cdot}37, \mu_2 = -0{\cdot}26$	+731	3·39	$\mu_1 = -3{\cdot}07, \mu_2 = +1{\cdot}42$	+442

* The directions of action of the resultant dipole moments are assumed to be parallel to the C=O axes.

In each case the μ's forecast in ref. 1 are used first, but since with acraldehyde and tiglaldehyde the observed polarities are in fact greater than these, we also show the ${}_{\mathrm{m}}K$'s expected when higher moments are taken for the two aldehydes in question.

Solute Conformations.—On the basis of Table 4, and the larger moments just mentioned, present measurements are consistent with a view that the solutes are mixtures of planar *s-trans-* and *s-cis*-isomers in proportions as follow:

Aldehyde	Proportions *s-trans* : *s-cis*	$10^{12}{}_{\mathrm{m}}K$ (calc)	$10^{12}{}_{\mathrm{m}}K$ (obs)	μ (D) (calc)	μ (D) (obs)
Acraldehyde *	4 : 1	387	385	$2{\cdot}8_4$	$2{\cdot}8_8$
Crotonaldehyde	23 : 1	738	738	$3{\cdot}4_3$	$3{\cdot}4_4$
Methacraldehyde	1 : 1	293	299	$2{\cdot}6_8$	$2{\cdot}7_2$
Tiglaldehyde	18 : 1	716	716	$3{\cdot}3_8$	$3{\cdot}3_8$

* Were the moments of *s-trans-* and *s-cis*-acraldehyde closer than assumed in Table 4, conclusions would not be greatly affected; *e.g.*, with μ = *s-cis* 2·70 and *s-trans* 2·90 (D), the calculated ${}_{\mathrm{m}}K$ and μ_{apparent} for a 4 : 1 *s-trans* : *s-cis* mixture are 391×10^{-12} and 2·86 (D), respectively.

From their molar Kerr constants, therefore, acraldehyde, crotonaldehyde, and tiglaldehyde appear to adopt predominantly the *s-trans*-conformations; qualitatively such a conclusion is in harmony with most of the previous relevant work. Acraldehyde vapour is reported [12] as 98% *s-trans* from its microwave spectrum, while from electron-diffraction studies Mackle and Sutton [13] suggested that at 35° the *s-trans* : *s-cis* ratio lay between 3 : 1 and 6 : 1; by the last-named technique, however, crotonaldehyde at 70° seemed [13] to show a ratio of *ca.* 1 : 1, in contrast to the indications (dipole moment,[1] ultraviolet spectra,[14,15] ultrasonic absorption,[16] etc.) afforded by solutions at room temperatures. Tiglaldehyde, on spectroscopic [15] and dipole-moment [17] evidence, has been considered as *s-trans*. Estok and Dehn [17] listed methacraldehyde as *s-trans*, but Forbes and Shilton [15] thought it existed to an appreciable extent in *s-cis*- and/or non-planar *s-trans*-conformations, citing infrared absorption intensities in support.

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

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[15] Forbes and Shilton, *J. Amer. Chem. Soc.*, 1959, **81**, 788.

[16] de Groot and Lamb, *Proc. Roy. Soc.*, 1957, *A*, **242**, 36.

[17] Estok and Dehn, *J. Amer. Chem. Soc.*, 1955, **77**, 4769.